AMERICAN
DYESTUFF REPORTER

VOLUME XXII | MAY 8, 1933 | NUMBER 10

Mechanism of Detergency

Properties Required in Concentrated Soap Solutions

By P. L. MANN

The properties of a given compound which determine its efficacy as a detergent are not yet fully understood. Concentrated solutions of soap are claimed to be good detergents because of their efficient wetting out and emulsifying ability. Soap solutions possess fairly high viscosity and low surface tension, and this fact enables them to form stable films of foam. Because of the tendency of the soap to be absorbed at the solid interface, together with the attendant low surface tension and low interfacial tension of the solution against the solid surface, it can penetrate into fabrics.

THE removal of fat, grease, etc., from textile fibers and fabrics in theory and practice involves the principles of molecular physics. The mechanism of a detergent is such that one part of the molecule dissolves in the hydrocarbon impurities, while another part of the molecule dissolves in water, in consequence of which the detergent acts as a linkage between the hydrocarbon and the water, and thus enables the fatty substance to be removed.

Typical detergents of this type are the sodium or potassium salts of stearic acid $CH_3(CH_2)_{16}COOH$ or palmitic acid $CH_3(CH_2)_{14}COOH$, the carboxyl group of which dissolves in the water while the hydrocarbon chain dissolves in the fatty substance. The water molecules associated with the carboxyl groups at one end of the soap molecules are then pulling at the soap molecules, and these being associated with the hydrocarbons of the fat globule are pulling in turn at the latter, with the result that the fat globule is split up and removed.

Considerable attention is being paid at the present time to methods of measuring more precisely the actual detergent power of a soap. A primary factor in this is its wetting power, for on this depends the other powers of dealing with dirt in any form. There is now little difficulty in estimating this wetting power very definitely by measuring the surface tension of a soap solution or its drop number. Another method, more closely related to actual working conditions, is to estimate the "sinking" or "immersion" time of an article to be washed.

Wetting out agents may be distinct from emulsifying agents. In certain cases the absorbed hydrocarbon residue is not large enough to promote dissolution of any organic substance but is only sufficiently large to wet the surface. It is often necessary to increase the wetting power of a soap solution, especially when dealing with greasy or oily dirt which greatly obstructs this particular action of a soap and tends to make it almost inoperative. For instance, it is well known that in the various processes of water-proofing textiles, water-insoluble fatty compounds are used. In dealing with such substances present in foreign matter it is necessary to incorporate or use with the soap a fat-solvent which thus acts indirectly as a wetting agent.

The next most important property in a detergent is emulsifying power. This is, in fact, the essential part of the cleansing process, and is accompanied also by a dispersion power which tends to break down or disintegrate the foreign substances to be removed. The actual mechanism of emulsification is extraordinarily complex. The emulsifying agent serves to inhibit the coalescence of the internal phase and does not necessarily determine the degree of dispersion reached.

Attempts to measure accurately the emulsifying power of a soap by determining the resulting whiteness of artificially soiled fabric by a soap solution of optimum concentration have not yet been altogether satisfactory, but research is being continued with a view to overcome some of the difficulties.

The effect of rise in temperature is, in general, to make emulsification easier. Reduction in viscosity is obviously a factor concerned. The main interest, however, lies in the relation of temperature to the interfacial tension and the adsorption of the emulsifier at the interface. A rise in temperature is usually accompanied by a decrease in the interfacial tension, a condition favorable to emulsification.

The ultimate stability of an emulsion depends on several factors. Enhancing stability will be (1) fine dispersion of the globules, (2) a minimum difference in the densities of the two phases, (3) a viscous continuous phase and (4) a stable film around the globules. For the last factor, time may be necessary to permit adequate

adsorption of the emulsifying agent, accompanied in some cases by de-solution due to desolvation.

The conclusion to be reached, therefore, is that a given emulsifying agent plays two parts (1) it permits easy dispersion owing to a reduced interfacial tension, and (2) it may promote stability after its adsorption, assuming the absence of disturbing factors such as chemical change or such physico-chemical alteration as leads to desolvation.

Linked with the property of emulsification is that of adsorption and lathering, by which the dirt particles, loosened and partly removed by emulsification, are finally "adsorbed" and carried away with the lather and in the subsequent rinsing. The washing process is thus essentially a matter of physical and colloidal chemistry and a better understanding of the way in which a soap solution acts has been gained by recent progress in research on colloids.

In addition to these essential qualities of a soap there are other factors to consider, one of which is stability in hard water. A soap which is not stable forms insoluble lime soap and other compounds which are left in the interstices of the fabric and cause unpleasant discoloration and smell. These "lime soaps" are somewhat sticky and glutinous and contaminate cleaning processes, giving trouble in dyeing, bleaching and finishing. It is also desirable that a soap should be stable with acid and that it should not discolor the wash or have other undesirable effects.

The practice of adding some form of alkali to a soap solution to increase its detergency is not uncommon. It is believed that this added alkali suppresses hydrolysis of the soap, assists in lowering the surface tension of the bath, and serves to adjust the pH value of the bath to a suitable range to stabilize the suspension or emulsion.

The special addition of alkali, such as soda, has received considerable attention in this country, and it has been found that, for best results from a detergent point of view, a certain definite hydrogen ion concentration is essential no matter what alkali is used. This does not mean, however, that these various forms of alkali are equally effective in adding to the cleansing power of a soap. The assumption that the detergent power rises parallel with the decrease in surface tension of the soap solution as produced by addition of alkalis or other substances is not necessarily correct.

Recent investigations have proved that the addition of an alkali may not always increase the detergent power of a soap solution. For example, all additions of borax decrease the detergent power. But it must not be concluded that this compound is useless as a washing agent, for under certain conditions it adds to the effectiveness of other alkalis when incorporated with a soap. The advantages obtained, however, are up to a certain optimum maximum pH as with further additions the detergent properties are adversely affected. The optimum pH is 10.7 and to secure this it is necessary to add 0.6 per cent of caustic soda, or 6.4 per cent of sodium phosphate, or 16.2 per cent of soda ash.

NEW PATENTS

(*Abstracted by S.O.C.M.A.*)

Metal Compound of Azo-Dyestuffs and Process of Making Same. (Comprises treating a mixture of different o-hydroxy-azo-dyestuffs, with trivalent compounds of chromium; suitable for dyeing wool, silk or cotton and also dyeing or coloring leather, varnishes and other materials, yielding bluish tints.) Fritz Straub, of Basel, and Hermann Schneider and Heinrich Bernhard, of Riehen, near Basel, Switzerland, assignors to Society of Chemical Industry in Basle, of Basel, Switzerland, No. 1,887,602, Nov. 15, 1932.

Vat Dyestuff. (As a new article of manufacture, 3.4.8.9-dibenzopyrene-5.10-quinone containing about one atom of bromine and three atoms of chlorine, dyeing cotton yellow shades from a violet red vat.) Max Albert Kunz, of Mannheim, Georg Kraenzlein, of Frankfort-Hochst-on-the-Main, Karl Koeberle, of Ludwigshafen-on-the-Rhine, Martin Corell, of Frankfort-Hochst-on-the-Main, Erich Berthold, of Ludwigshafen-on-the-Rhine, and Heinrich Vollmann, of Frankfort-Hochst-on-the-Main, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,887,812, Nov. 15, 1932.

Manufacture of Strongly Basic Azo-Dyestuffs. (By treatment of nitrated amines with chloracetyl-chloride and a body of the pyridine group; dye tannin-mordanted cotton and weighted silk yellow to red to orange shades fast to washing and light.) Achille Conzetti, of Basel, Switzerland, assignor to the Firm: J. R. Geigy S.A., of Basel, Switzerland, No. 1,887,995, Nov. 15, 1932.

Manufacture of Strongly Basic Azo-Dyestuffs. (A division of above patent No. 1,887,995). Achille Conzetti, of Basle, Switzerland, assignor to J. R. Geigy, S.A., of Basel, Switzerland, No. 1,887,996, Nov. 15, 1932.

Manufacture of Azophthalein Dyestuffs. (Consists in condensing a diethylaminohydroxybenzoylbenzoic acid in equimolecular proportions with a monoazo-dyestuff from resorcinol; genuine mordant dyestuffs which, when after-treated on the fiber with metal salts, yield fast valuable dyeings of blue to greenish-blue and red to brownish-red tints.) Adolf Krebser, of Basel, Switzerland, assignor to the Firm J. R. Geigy S. A., of Basel, Switzerland, No. 1,888,002, Nov. 15, 1932.

Azo-Dyestuffs Containing Chromium and Process of Making Same. (Dye fibers of animal, vegetable and artificial origin, and varnishes, blue to grey tints.) Fritz Straub, Walter Anderau, and Hans Mayer, of Basel, Switzerland, assignors to Society of Chemical Industry in Basle, of Basel, Switzerland, No. 1,888,516, Nov. 22, 1932.

Theories of Cotton Structure

Explanations of the Properties of Cotton Which Form the Basis of Modern Research

THE details of the structure of the cotton fiber (or hair) are still far from known and the issue is somewhat confused by the fact that each investigation in the field tends naturally to a view supported by the evidence with which he is most familiar. This, of course, causes some apparent disagreement in the literature, but there are general views which are pretty well accepted.

While the micellar theory of the structure of cellulose seems quite firmly established, it is not yet universally accepted. The following notes on cotton are based very largely on a paper by F. T. Pierce, which has probably not been available to many readers of the DYESTUFF REPORTER. This paper gives some important views on the interior structure of the cotton hair based on very extensive research. It has been supplemented by ideas from other sources and comments by the present writer, in order to bring some of the points into line with later work.

It seems safe to assume that Pierce's views reflect the findings of the British Cotton Industry Research Association and therefore should carry much weight in any consideration of this subject.

The most noticeable thing about the fine structure of cotton is the spirality in the cell wall, which reverses its direction at irregular intervals. This structure with its reversals produces convolutions, or "twists," which distinguish cotton from other common fibers and which are usually supposed to contribute much to its practical usefulness.

This spiral structure appears to be continuous from the primary wall to the lumen, that is, through the whole thickness of the wall of the hollow cell or hair. Even the twenty-five or thirty growth rings in the cell wall do not represent real interruptions in the structure. It is continuous even in a molecular sense.

When oxidized, swollen in sodium hydroxide, and stained with Congo Red, the cuticle shows regular markings at right angles to the direction of the spirals, and changing as it changes. These are evidently in a principle plane of the crystal structure as revealed by X-ray analysis (and indicate where destruction may begin).

Chemical Nature of Cellulose

It now seems from chemical evidence to be well established that cellulose is correctly represented by chains of cellobiose residues, each of the latter consisting of two glucose residues and each of these in the form of a six-atom ring (five carbon and one oxygen). This is the view now common in the literature.

While the structure is crystalline, it is also somewhat irregular, the chains being of varied and indefinite lengths. While in general very stable, the chains can be easily broken chemically, and the groups at the end, normally aldehydic and reducing in nature, may be more or less accessible to reagents.

There is no evidence of two types or two phases of cellulose. However, it should be made plain here that the outer layer of the cotton fiber is different in some way from the main part of the wall and acts unlike ordinary cellulose. Pierce evidently refers here to the inner structure which has been interpreted as consisting of separate crystallites embedded in a matrix of amorphous cellulose. This amorphous cellulose has heretofore furnished a convenient explanation of observed phenomena, but there appears to be little if any real evidence for it.

As an aside, the present author would argue that if any of the substances is amorphous it is not cellulose, because it is the particular arrangement of carbon, hydrogen, and oxygen atoms in the form that we now recognize as crytalline that makes them cellulose. There may be minute mixed-up portions of crystallites which cannot be recognized as crystalline, but if they are still cellulose they must be actually crystalline. This, of course, falls in line with the modern findings that many colloidal or supposedly non-crystalline materials do have an underlying structure or orientation which is sufficient so that they cannot be considered truly amorphous.

The Question of Micellar Structure

From the character of the interference spots, it appears that the repetition of the crystal planes is interrupted at small intervals, which are usually interpreted as a measure of the crystallites or micelles. But, it is also claimed that, since the structure only approximates to crystalline perfection, it may be even more in accord with the evidence that these are merely local discontinuities in the structure, which would nevertheless have the same effect on the X-ray diagram as if they were micellar boundaries. In other words, the micellar theory has not been unanimously accepted.

On the other hand, observations recently made by means of that very valuable new research tool, the Spierer lens, appear to confirm the micelle theory and the structure that is indicated by X-ray methods. Thiessen considers that it is clearly shown that cellulose fibers such as cotton and ramie are built up of micelles.

The usual diagrammatic representations show the micellar structure as a brick wall type with the bricks breaking joints or overlapping. The strength of cellulose is attributed to the attractions between the sides of these overlapping micelles.

The Spierer photographs so far available do not clearly show such overlapping. There are parallel lines which are taken to be chains of micelles and they show minute indentations (better seen directly than in reproductions). These are interpreted as representing the micelles in the chains, although their actual lengths cannot be seen from the photographs.

Contrasted to this is the view, still held, that the spiral elements in cotton are continuous from one end of the hair to the other unless interrupted by accident. And, no reason seems to have been presented to show why cellulose should grow into discontinuous micelles or crystallites.

Swelling Effects

Water can penetrate the cotton hair structure without changing the X-ray diagram. The most obvious explanations is that it does not penetrate the crystallites, which would be the case if the water did not force itself between the atoms in the crystal units. If it did enter the crystallites, the atoms would be expected to be forced apart or into new positions and thus change the dimensions of the X-ray diffraction diagram.

However, the amount and the effects of the absorbed water seem to indicate that it does penetrate throughout the crystal structure. This is certainly true of swelling alkalies and esterifying acids which also fail to produce any continuous contraction of the diffraction pattern. Such constancy of diagram might be maintained if the water were taken up between the concentric layers and did not affect the lengthwise or tangential bonds or cohesive forces. The change in dimensions on swelling accords with this view.

Strong bases cause swelling or even solution of the cellulose. The size of the particles dissolved or (more properly) dispersed, depends on the relation between the dispersing force and the strength of such flaws as are irregularly scattered through the structure. Again Pierce states that there is no reason to suppose pre-existing boundaries of individual particles in the substance of the fiber, which is to say that the conception of micellar units is an unnecessary complication.

It all boils down to a choice between pre-formed micelles whose average size corresponds quite well with the size of particles in cellulose solutions (dispersion), or particles of this size that result from accidental points of weakness in the hair structure which break up in the dispersing agents.

Instead of the concept "molecule" it now seems much more fruitful to consider the little "link," the $C_6H_{10}O_5$ which is usually written in parenthesis, and the little "chain" represented by some number of these links connected in a line and expressed by the "n" in the usual cellulose formula.

Cohesive Forces

The elastic properties indicate that the lengthwise cohesive forces are virtually unaffected by moisture. On the other hand, the spirals seem to cohere radically through hydroxyl groups which are very sensitive to moisture. The properties are well accounted for by the assumption that each glucose residue contains one hydroxyl that is mainly responsible for radical cohesion and can hold one water molecule as "water of crystallization," (which does not seem to be exactly the same thing as oriented adsorption although probably indistinguishable from it in effect).

The lengthwise bond is supposed to be the oxygen bridge (—O—) formed by dehydration when the soluble carbohydrate condenses to the solid glucose residue (or biose) on the cellulose wall which has already formed. The next step is coherence as concentric sheets through the hydroxyl groups as already mentioned. The layers are laid down in the presence of water and possibly connected first through water molecules

——OH—HOH—HOH—HO——

Upon drying, the molecules cohere directly.

An interesting point brought out by O. L. Spousler is that the glucose units, while flat in their general outlines and, of course, drawn flat on paper do not lie flat in the cell but at a slant of about 45°. Thus at the growing surface on the inside of the hair wall the edge is the part exposed to the protoplasm within the cell. Growth evidently takes place along a line of hydroxyl groups on this edge. This would seem likely to the present writer to leave a very active cellulose surface inside the fiber lumen when growth ceased, unless it were in some way "saturated" by other materials present at that time.

In conclusion, little can be said except that it is unfortunate but still true that we cannot definitely agree which are the facts. It is, however, possible to approach cellulose research with ideas much more useful than we had even a few years ago.

Main References

Reinhardt Thiessen. Ind. Eng. Chem. *24*, 1032 (1932).

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The Effect of Salt on Boil-off in Silk Soaking

By **RALPH HART**
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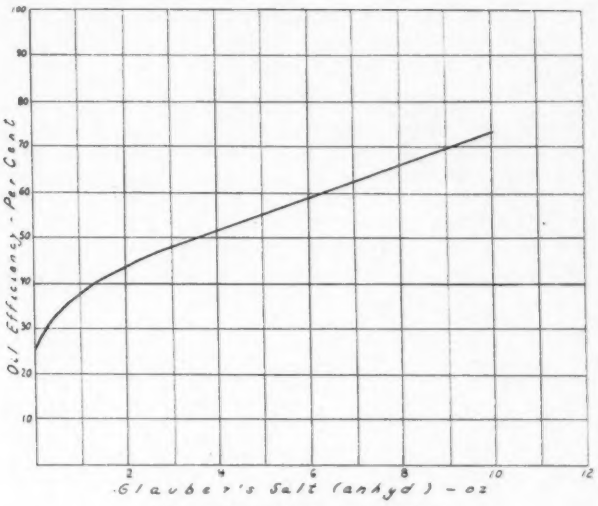

Fig. 1.—Effect of Salt on Oil Efficiency.

A RECENT article by Herbert C. Roberts on the use of salt in the silk-soaking bath (Silk Digest Weekly, Vol. 24, p. 24, 1933), should prove of interest to throwsters who believe in economizing at every opportunity. As a result of an investigation, Roberts concludes that common salt (NaCl) will not cause tender silk nor will it set the tint, provided a total of about 5 oz. is used per 100 lbs. of silk soaked in a bath of 70 gals. In the case of more fugitive tints a larger quantity of salt is permissible. Moreover, it was found that wherever salt produced oily silk, it was traced to an initial high salt content in the water used (often Zeolite-treated) so that the addition of more salt produced an excess. It was also found that if the total salt content per soaking was kept below 6.5 oz., no excess soap was required to degum the silk.

Roberts also claims that soluble silk oils on the market may contain as much as 4.5% salt, mostly sodium sulfate, or equivalent to about 11 oz. of salt per soaking. As a matter of fact, very little of the salt found in the ash of a well made sulfonated oil compound is present as such in the original oil, the amount rarely exceeding 1.0%. While Roberts points out the negative advantages of adding salt to the soaking bath, he does not indicate to what extent the throwster may benefit by its use. The present writer some time ago investigated quantitatively the effect of salt on boil-off and oil efficiency and believes that the data, though not complete, may help partly to supply this information.

The investigation consisted of making laboratory soakings, using two skeins of silk for each soaking but otherwise duplicating practical conditions as closely as possible, with various quantities of anhydrous Glauber's salt, and determining indirectly the boil-offs of the soaked silk. Boil-off was found in the following manner: The total per cent solids in the bath before and after soaking were determined; the former gave the total amount of oil used, the latter (by assuming that bone-dry silk absorbs its own weight of liquor after soaking and centrifuging) gave the amount discarded, and the difference the amount of oil left upon the silk. This method of calculating boil-off was found to check closely with actual boil-off determinations, provided the liquor left in the silk is approximately the assumed amount, and is recommended for rapid work or where there are many such tests to be made.

Table I shows the effect of salt on the oil efficiency and the boil-off. The action of salt on the oil efficiency is also shown in Figure I. The table and graph are based on 100 lbs. of silk, soaked in 60 gals. of water containing 12 lbs. of soluble oil, 1.5 lbs. of soap and various amounts of sodium sulfate. It will be noticed that when the salt content was raised from zero to 10 oz., the oil efficiency increased from 25.4 to 73.4%, or almost three times as much, and the boil-offs increased from 21.1 to 25.8%, respectively. These figures very clearly indicate the sensitivity of the soaking emulsion to being broken by the addition of salt, with a consequent gain in boil-off and oil efficiency. The data given in table I should be considered as only approximate, since the results would naturally be affected by the stability of the oil emulsion, acidity of the silk, hardness and total solids in the water, etc., factors which were not investigated during this work.

The saving in oil by the judicious addition of salt may be judged by referring to table II, in which the boil-offs and oil efficiencies are given for soakings containing various amounts of oil but no salt. It will be noticed that the exhaustion of the bath, as shown by the drop in concentration after soaking, is small when compared with the results in table I, where salt was used. The oil efficiency in the absence of salt was never above 30%, and the boil-off only about 23.0% even with 24 lbs. of oil. The same boil-off is possible with 5 oz. of salt and only 12 lbs. of oil, or a saving of 50% in the amount of oil. In practice a somewhat better oil efficiency than shown in table II is

Table I

Effect of Glauber's Salt (Anhyd.) on Boil-off and Oil Efficiency*

No.	Concn. Soaking Bath, Per Cent Before	After	Glauber's Salt (Anhyd.) Oz.	Boil-off (Calcd.) Per Cent	Oil Efficiency, Per Cent
1	2.32	2.11	0	21.1	25.4
2	2.33	1.66	2	22.7	41.8
3	2.37	1.41	4	23.6	51.3
4	2.36	1.21	6	24.2	58.0
5	2.42	1.00	8	25.2	66.1
6	2.42	0.79	10	25.8	73.4

*Factors remaining constant during the experiments:

Silk (air dry)	100 lbs.
Water	60 gals.
Soluble Oil	12 lbs.
Soap	1.5 lbs.
Method	tub
Temperature	85-90° F.
Time	overnight

Table II

Effect of Oil on Boil-off and Oil Efficiency*

No.	Soluble Oil, Lbs.	Concn. Soaking Bath, Per Cent Before	After	Boil-off (Calcd.), Per Cent	Oil Efficiency, Per Cent
1	12	2.32	2.11	21.1	25.4
2	15	2.78	2.54	21.7	25.2
3	18	3.15	2.82	22.2	26.6
4	21	3.38	2.96	22.6	28.2
5	24	3.73	3.22	23.2	29.2

*Note: other factors the same as in Table I.

Table III

Outline for Calculating Boil-off and Oil Efficiency

Soaking Formula:	
Silk	100 lbs.
Moisture 10.0% (assumed)	
Boil-off 18.5% (assumed)	
Water	486.5 lbs.
Soap	1.5 lbs.
Oil	12.0 lbs.
Total weight of bath	500.0 lbs.
Concentrations:	
Solids before soaking	2.32%
Solids after soaking	2.11%
Take-up:	
Bone-dry silk	90 lbs.
Waste liquor (500-90*)	410 lbs.**
Solids before soaking (2.32% x 500)	11.60 lbs.
Solids after soaking (2.11% x 410)	8.65 lbs.
Take-up (diff.)	2.95 lbs.
Boil-off:	
Bone-dry soaked silk (90 + 2.95)	92.95 lbs.
Gum (90 x 18.5%)	16.65 lbs.
Gum and take-up (16.65 + 2.95)	19.60 lbs.
Boil-off (19.60/92.95)	21.1%
Efficiency:	
Oil efficiency dry basis (2.95/11.60)	25.4%

*Weight liquor absorbed by silk.
**Moisture in the silk has been disregarded.

usually obtained, due to the presence of some salt in the oil or to other factors tending to de-stabilize the emulsion.

In table III is outlined a method for calculating the oil efficiency and boil-off for experiment No. 1 in table I, according to the scheme already mentioned.

It was pointed out in a recent publication that judicious use of salt in the silk soaking bath is not detrimental to the process; in this paper it is shown that a considerable saving in the amount of oil (by the tub method) may be effected by its proper use. A rapid method for determining boil-off is likewise outlined.

Joint Chemical Meeting

A joint meeting of the Society of Chemical Industry, the American Chemical Society, the Electrochemical Society and the Societe de Chimie Industrielle will be held on May 12th at 8:15 P. M. at the Chemists' Club, 52 East 41st Street, New York City. The speaker will be Dr. Gustav Egloff of the Universal Oil Products Co., Chicago, who will present a paper entitled "Synthetic Petroleum Products." Preceding the meeting a dinner will be held at the Club.

Herrick & Voigt Move Office

Herrick & Voigt have moved their New York office to 21 West Street. The new telephone number will be BOwling Green 9-2582 and 3.

Determination of Acids in Wool

With Particular Reference to Dyed Goods*

By S. R. TROTMAN, M.A., F.I.C., and G. N. GEE

The determination of acid in woolen goods, both undyed and dyed, is often a matter of considerable importance. There may be present sulfurous, sulfuric, hydrochloric, acetic, or formic acids. Both sulfurous and sulfuric acids are found in stoved goods, while any of the acids mentioned may occur in dyed samples. The determination of acid is affected by the facts that wool has basic properties and adsorbs acids from their aqueous solutions. This acid is held tenaciously.

HARRISON (*J. Soc. Dyers & Colourists,* 1918, *34,* 27) found that when wool containing sulfuric acid was washed repeatedly with boiling water, it was free from acid after the 23rd washing. We have repeated this experiment and found that, although the wool was apparently free from acid, the whole of the added acid could not be recovered from the washings. This seems to agree with the experience of Hirst and King (*J. Textile Inst.* 1926, *20,* T101). Extraction with alcohol is unsatisfactory because other substances besides acid are removed. For these reasons, indirect methods of determination must be employed, e.g. (1) treatment with N/10 ammonia and titration of the unneutralized ammonia; (2) treatment with N/10 sodium bicarbonate followed by back titration; (3) digestion with magnesium carbonate and determination of the magnesium salt formed; (4) the terephthalic acid method of Hirst and King (*J. Soc. Dyers & Colourists,* 1926, *42,* 171); (5) the method of Woodmansey (*ibid.,* 1918, *34.* 172).

In the experiments to be described, we have made comparative trials of these methods. Certain modifications are suggested together with new methods of analysis, viz.—(1) the substitution of triethanolamine for ammonia; (2) distillation with sodium acetate; (3) distillation with calcium carbonate.

The experiments were made with purified wool and with commercial samples of dyed and undyed wool.

Purification was effected by the method used by Hirst and King (*loc. cit.*). The wool was digested at 80° C. with dilute hydrochloric acid to decompose soaps, then washed with distilled water, dried and extracted with benzene in a Soxhlet extractor, after which it was washed again with water and treated with small quantities of dilute ammonia until neutral, washed with water and dried at about 80° C. It will be noted from the figures given later, that it is very difficult to obtain wool which is absolutely acid-free, the acidity of different samples varying from 0.11 to 0.29% calculated as sulfuric acid. An alternative method gave rather better results. It consisted of the following operations—(1) extraction with ethylene trichloride; (2) digestion with hydrochloric acid, washing with water and drying; (3) extraction with ethylene trichloride; (4) extraction with alcohol; (5) washing with water; (6) neutralization with ammonia; (7) washing with water and drying.

The dry wool was tested by the sodium bicarbonate and sodium acetate methods and found to contain 0.098% acid calculated to sulfuric acid.

Methods of Washing—Some of the methods used involved repeated washing with water, requiring much time and attention. Attempts were made to do this by means of a continuous extractor shown in Fig. 1.

(A) is a glass tube closed at both ends with rubber bungs through which pass glass tubes leading to a water container (B) and a collecting vessel (C). A tap (E) regulates the rate of flow of water through the extractor. The wool is placed in the tube between two plugs of glass wool and packed tightly so that no channels can be present. The extractor is immersed in a beaker (D) containing water heated nearly to the boiling point, and water is allowed to enter the extractor until the wool is wetted down. The tap is then closed and the apparatus allowed to stand for an hour. After this, the tap is opened until the water runs through, the rate of flow being controlled so that there is a distinct interval between two successive drops entering the receiver. The water in the beaker is kept at the boiling point by a Bunsen burner and the extraction continued until 1 liter has been collected. It was found to be impossible to remove the whole of the acid or alkali present in wool by this method, and the following method was adopted (Fig. 2).

The wool to be washed is placed in the tap funnel on a plug of glass wool. The tap is closed and hot water added. After a time the tap is opened and the liquid

*J. Soc. Dye. & Col.

sucked out, the wool being pressed down with a glass rod flattened at one end. When no more liquid can be pressed out, the tap is closed and the process repeated.

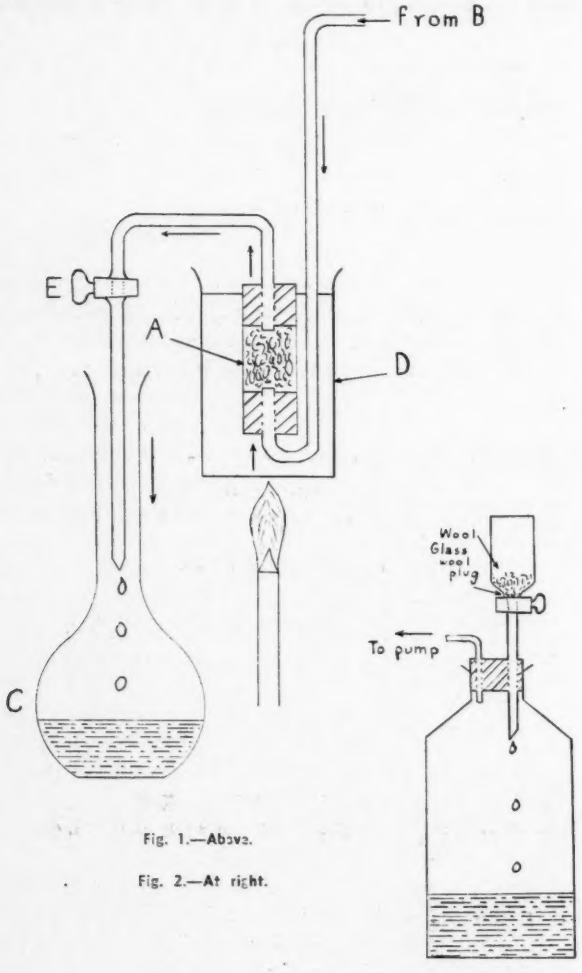

Fig. 1.—Above.

Fig. 2.—At right.

The Ammonia and Triethanolamine Methods—In the ordinary method, a weighed quantity of the wool is placed in a stoppered bottle together with a definite volume of N/10 ammonia, and allowed to stand for 12 hours. The residual ammonia is then determined by titrating a portion of the liquid. The method is unreliable owing to adsorption of ammonia by the wool. Hirst and King (*loc. cit.*) found that this amounts to 0.25% on the weight of wool used, which gives an error of about 0.7% in the final result. They suggest that the introduction of a correction factor makes the process reasonably accurate although this factor varies for different kinds of wool. We found that triethanolamine was more suitable than ammonia, as it is not adsorbed to so great an extent. Samples of wool were treated with N/10 solutions of both ammonia and triethanolamine and titrated. The results obtained were—

Expt.	% H_2SO_4 by Ammonia	% H_2SO_4 by Triethanolamine
1	1.04	0.73
2	2.62	2.19
3	0.96	0.48

Some neutral wool treated with a known quantity of sulfuric acid and dried gave with triethanolamine—

% H_2SO_4 added	% H_2SO_4 found
2.9	3.2
4.0	4.3

Triethanolamine has also an advantage over ammonia in that the wool can be washed with hot water which cannot be done without loss in the case of ammonia. 5 G. of neutral wool were soaked overnight in N/10 triethanolamine, the liquor was then decanted and the wool transferred to the tap funnel of the apparatus described above, where it was washed twelve times with hot water. The liquid and washings were then titrated, the difference between the volume of triethanolamine solution used and that recovered being calculated to sulfuric acid. This amounted to 0.11%, indicating that practically the whole of the triethanolamine had been removed. It was found also that when the same method was used with ammonia, substituting cold for hot water, the results obtained were much more accurate than those given by the ordinary method. Thus—

Volume of N/10 Ammonia added	Acid found calculated to H_2SO_4
50 cc	0.19%
100	0.20
150	0.20

The Sodium Bicarbonate Method—This method was proposed by Meunier and Rey (*Rev. Gén. Mat. Col.* 1924, *28*, 66). A weighed quantity of the wool is soaked for 24 hours in 200 cc. N/10 sodium bicarbonate. The liquid is decanted and the wool washed four times with 50 cc. water. The liquor and washings are boiled with a known excess of N/10 hydrochloric acid cooled, and titrated with N/10 sodium hydroxide in presence of phenolphthalein. Four washings with water do not remove all the excess of bicarbonate, but with repeated washing at the pump the method gives practically the same results as triethanolamine. It is not essential that the liquid should be boiled with sulfuric acid before titration.

The Magnesium Carbonate Method—This depends upon the fact that although wool adsorbs both acids and alkalis, neutral salts can be removed from it readily by washing with water. It is useful in the analysis of dyed samples, since no color is extracted. A weighed portion of the sample is heated in water containing finely powdered magnesium carbonate in suspension. The liquid is decanted and the wool washed with water. The liquid and washings are diluted to a definite volume and the combined sulfuric acid determined in a portion of the solution by precipitation with barium chloride. When the

(Continued on page 316)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

MAY 8, 1933

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The Utility of

Chromium Plating in Calico Printing*

By **JOHN B. DICK**
Superintendent, Norwich Branch, The U. S. Finishing Co.

IN ORDER that a person may properly appreciate the advantages derived from the chromium plating of copper printing rollers, it is necessary that he understand some of the difficulties encountered in the use of plain copper rollers in calico printing.

Anyone who has used copper printing rollers knows that one of the chief properties of copper, namely, the ease with which it can be manipulated, is also its chief drawback.

It is comparatively easy for an experienced engraver to correct on copper those errors which are bound to creep in during the engraving process. A section of the design may be "missed" during pantographing; extra engraving may be put on a roller where it should not be; or a roller may be damaged while being handled in the Engraving Shop or in the Print Room. A skillful engraver can correct these defects with comparative ease, although at times the correction may be a rather lengthy job. Copper can be cut easily with a "graver" to put in the missing parts of the design; it can be "plugged" and smoothed off to eliminate extra sections of engraving, and it can be hammered, plugged or cut in order to repair damages caused by careless handling. It is a beautiful metal to work with in this respect, and it is a thing of beauty to see the ease with which a competent "roller-man" makes the necessary corrections on a roller.

* Presented at meeting, R. I. Section, Feb. 24th.

But after a copper roller has been placed in a print machine, the ease with which it can be cut and altered immediately becomes its chief drawback—with two exceptions. The exceptions are those instances when it is necessary to polish a roller to reduce the depth of the engraving on it, or when it is necessary to "pare" rollers, chiefly in multicolor patterns, in order to eliminate grains in a print due to the definite tendency of cotton cloth to pull in the successive narrower while it is being pulled through the successive rollers of a print machine. In these cases it is still an advantage to be dealing with plain copper rollers.

However, when the copper rollers have been properly engraved and whatever touching-up of the engraving as was necessary has been done, the base metal of the roller becomes base indeed.

As you are aware, the ordinary calico printing machine applies its color in the following manner: Thickened color is supplied to the roller by means of a furnisher roll or brush. The entire surface of the roller, both plain and engraved, is smeared with this color mass and as the roller revolves, the color on the plain portion of the roller is wiped off by means of a sharp steel doctor blade. The blade is set at an angle to the roller and as it is necessary to get a very close contact with the plain surface of the printing roller in order to prevent any but the thinnest film of color remaining on the plain surface, considerable pressure is applied to the blade by means of weights attached to each side of the doctor blade holder, or shear. If a roller is engraved just right, there is left on the etched sections fine lines of copper which are level with the plain surface of the roller. The fine lines, or "tops," of the engraving, when they are level with the plain surfaces, furnish a support for the doctor blade over which it rides without dipping into the valleys of the engraving and removing some of the color which should be applied to the cloth. This provided, of course, that the doctor blade has been properly set on the roller.

However, the art of etching copper is an extremely delicate one. When nitric acid is used, etching takes place in a very short space of time and even a slight error in judgment on the part of the etcher will result in a roller being etched not quite enough or just a trifle too much. When the former occurs, the "teeth marks" familiar to most of you show up on the cloth as faint white lines where little or no color has been applied, and these must be eliminated if a satisfactory print is to be obtained. When the latter occurs, the support for the doctor blade that is provided by the roller that is engraved exactly right is no longer present and the blade, because of the pressure on it, dips down into the engraving and scrapes out some of the color which should properly be applied to the cloth.

If this dipping be slight, probably no harm will come from it, especially if the yardage printed on the pattern is small. However, the damage done by a dipping doctor blade is progressive. The blade traverses sideways as the roller revolves and its sharp edge has a decided cutting effect. Engraving that is slightly under the surface has what are known as rotten tops to it. The top edge, instead of being smooth is very rough and ragged and it takes comparatively little wear from the steel doctor to knock off the ragged tops and reduce the depth of the engraving to such an extent that "dragging" or digging out of the engraving is necessary to produce a satisfactory print.

Even with perfect engraving, there are a good many times when a roller is damaged during the printing process itself. There may be gritty material present in the color paste, in the cloth being printed, or in the back-greys used, which may become caught between the blade and the roller and scratches the plain surface of the copper to such an extent that it must be repaired to prevent the production of second quality goods. In the case of vat colors, very extensive rips, where the plain surface of the copper has seemed to have been actually torn out, have been caused where nothing more dangerous looking than light and heavy weights on the blade have seemed to be the cause of the damage. The damage caused from such rips usually requires a good deal of an engraver's time to repair.

From the above, I would not like to give the impression that there is nothing right about copper rollers, as far as their utility in a print machine is concerned. We all know that millions of yards have been printed and are being printed on plain copper rollers—and successfully printed. But all of us who are concerned with printing are intensely aware of the many shortcomings of plain copper in a print machine.

Fortunately, the chromium plating of copper rollers seems to be the answer to the printer's prayers in this connection. As it is applied after the engraving has been completed, it does not interfere with the utilization of all of the exceptionally good qualities of copper from an engraver's standpoint. Because of the extreme hardness of chromium and its excellent resistance to wear, it seems to be exactly what is needed to complement copper and make a chromium plated copper roller one which is immune to practically all the ordinary source of roller trouble in the printing process.

Rotten tops mean practically nothing to a chromium plated roller. The hard protective surface of chromium is usually sufficient to prevent the doctor blade knocking off the tops so that dipping does not occur. The ordinary grit that commonly scratches plain copper rollers has comparatively little effect on a plated roller. To be sure, plated rollers do get scratched, but it seems to take a considerable chunk of grit to do the job. Fine grit that would scratch straight copper has practically no effect on the chromium. Vat printing pastes, so far as my own experience goes, are absolutely incapable of producing

the common rip on a plated roller even though the color box may be loaded with lint and heavy weights carried on the blade.

Somewhat more than three years ago, we at the Norwich Branch of The United States Finishing Company were experiencing an epidemic of roller damages which, for want of a better term, we called "darts." We never found the cause of these defects and never could advance any logical explanation of the manner in which they were formed. They showed up in the shape of an arrowhead on the plain surface of our copper printing rolls. There seemed to be a small hole in the copper at the point of the arrowhead and fine scratches varying in length radiated from this point. When these darts were present on rollers which were printing relatively weak colors, we experienced no trouble from them, but when they formed on rollers printing strong colors, it was a different story. We were held up for hours on end repairing them.

At about this time we became acquainted with the chromium plating of copper rollers, and because of the promise which plating held forth to rid us of this problem, as well as the dipping of blotch rollers, which is always a problem in a drapery plant—and also because times were good in those days, it was comparatively easy to convince our officials that the installation of a plating plant would be a worthwhile investment.

In January, 1929, we started work on the plant and had it in operation within a short time.

Originally, we used a solution containing approximately 225 g. of chromic acid per liter and a 50/1 ratio of Sulfuric Acid. We used a current density of 1.3 amperes per square inch and plated anywhere from 20 min. to one hour. We received considerable advice concerning our plating procedure from Dr. E. K. Strachan of the Physical Chemistry Department of Brown University. Our chief source of information was a bulletin put out by the Engineering Research Department of the University of Michigan. At that time the authors of the bulletin held the opinion that in spite of the fact that United Chromium, Inc., had been granted patent rights covering the commercial application of chromium plating, it was not necessary to be licensed by this concern to plate legally. They held that the patents could not be defended by virtue of the fact that a good deal of the material that seemed to be the basis on which the patents were founded had been published in scientific magazines several years prior to the filing of the applications for the patents which United Chromium controlled.

Incidentally, later developments have seemed to establish beyond any doubt whatever the validity of the United Chromium patents. A series of court actions ending in January of this year in the United States Supreme Court has seemed to fully and completely justify their contention that commercial chromium plating, as it is commonly carried on today, cannot be carried on legally except under license from United Chromium, Inc.

However, at the time we were putting in our plant, we felt a license was not necessary and went ahead with our plans on that basis.

From the outset we encountered difficulties. Our first and most serious trouble came from a tendency of chromium plated rollers to scum in such a way that it was impossible for the doctor blade to properly clean the plain surface of the printing rollers. As a result we had innumerable delays, especially when printing Steam Black, on account of the thin film of black which was not cleaned off, discoloring the lighter colors applied in the same pattern.

We found that on account of this feature our printers became decidedly prejudiced against the use of plated rollers. We found that because of the dulling effect of chromium plate on engravers' tools and the necessity of developing a somewhat different technique in the repairing of rollers in the machine, due to scratches, etc., that our engravers did not take any too kindly to the innovation.

However, we had our chromium plating plant on our hands, representing a considerable investment, and some of us had an abiding faith in the great ultimate value of chromium plating as a printing aid. We "took our medicine" in the form of print machine delays but kept steadily at work in an effort to overcome the drawbacks of the plated rollers.

During this time we had been on very friendly terms with the representatives of United Chromium, in spite of not being licensed by them, and had received a good many valuable suggestions from them in connection with our plating problems. About the first of November, 1929, at a time when we seemed to be making no headway with our scumming problem, we decided to take out a license from United Chromium to get the benefit of their experience in the solution of our difficulties. We have never regretted it. While United Chromium did not solve the scumming problem—we still have it with us occasionally—their efforts coupled with our own definitely established the cause of the trouble and pointed the way towards its elimination.

Prior to taking out our license with them, we had been suspecting our plating procedure as the cause of the trouble. However, it continued after changing over to their plating solution. They use about 400 grams Chromic Acid/liter, whereas we had been using 225 grams. We found the chief source of scumming to be mainly in the surface of the copper roller before plating. A roller which might be perfectly satisfactory, as far as surface was concerned, when printing unplated, might give a good deal of trouble from scumming if used in a plated condition. We found that a very smooth surface on the copper was absolutely necessary if a satisfactory printing job was to be done by a plated roller, especially if a strong color were used on the roller.

As the chief line of work done by the Print Department of the Norwich Branch of The Finishing Company is the printing of draperies, we have occasion to use a great many and a great variety of rollers. In the past three years we have plated approximately 13,000 rollers, largely for our own use, and thus have had an excellent opportunity of observing the value of chromium plate.

Drapery patterns, as a rule, are large designs. Spans, or sections of engraving, vary in width from fine single-point line for stems to the full width of the roller for some blotches. There are usually several half etches in a pattern, some being half etches of one color on another and others being straight half etches on white. Expensive hand-engraved and photographically engraved rollers are very often incorporated in patterns of this type. Very fine pantograph engravings are used a great deal. In other lines of work, expensive milled jobs are common. Basic, Alizarine, Vat, Salt, Rapid Fast and Rapidogen colors are used. With all these types of engraving and colors, chromium plating affords a protection that is not approached by anything else I have experienced.

We have yet to see a properly plated blotch which has been dipped by a doctor blade. Halt etches, which used to be nightmares to use, with the frequent dragging they required, no longer trouble us in this respect. Fine and expensive engravings can be handled in the print machine like ordinary rollers, as far as doctor blades damaging is concerned. Vat colors are like any others, as far as scratches and rips are concerned. I've never seen a Vat color "rip" on a plated roller.

To be sure, plated rollers wear but the wearing is very gradual, except in weak spots in the plate. Besides that, when they do wear they can be very quickly detected as the color of the underlying copper shows through on the roller long before ordinary wearing damage becomes harmful. When copper does show through, the remedy is simple. The plate is stripped off by heating the roll with steam and revolving it in a 10% solution of Muriatic Acid. After removal of the plate, the roller is cleaned, replated, and as good as new again.

We still have occasion to drag blotches and half-etches, but not on account of dipping by the blade. Usually a plated roller that requires such treatment has had its engraving knocked down somewhat by a polishing stone prior to plating, or has been engraved with too fine a line for the cloth it is being used on. Our engravers experienced some difficulty at first in cutting through the plated surface while dragging, paring, but at the present time they handle these jobs very much as they would on plain copper, although it does require considerably more effort.

Most of us have a feeling that any plating would have a tendency to fill up fine engraving, but with chromium, at any rate, this is not the case. Chromium has a very low "throwing" power in plating. It is difficult to get it to plate around corners or into deep recesses. As a result, it deposits itself on those parts of the cathode that are nearest the anodes, which in the case of an engraved roller, are the tops of the engraving and not the bottoms. The U. S. Bureau of Standards claims that the chromium plated plates used by the mint in printing money produce sharper results than do the unplated plates. If your memory is good, you can probably recall that there is some rather fine engraving on a dollar bill.

We have had some very good opportunities of observing the excellent wearing qualities of chromium plated rollers. Patterns with spans of twelve inches and more have run over a hundred and fifty thousand yards without having the rollers with the large spans touched at all. Vat patterns running at very high speeds have run a quarter of a million without requiring any touching up of the rollers whatever.

You no doubt are interested in the actual plating plant and the method of handling rollers during the plating process.

Our equipment consists of a 2,000 ampere motor generator set which is hooked up to the plating bath. The bath itself is a welded iron tank lined with 6% Antimony Lead. It is 107 inches long on the inside and about 23 inches wide and 23 inches deep. It is equipped with temperature control coils, which also are made of 6% Antimony Lead, and are supplied both steam and water for the regulation of the temperature of the bath. This is maintained at 114° F. by means of a Foxboro controller recorder.

Along the sides of the tank are large exhaust ducts which effectively carry away all spray from the bath. This spray collects in the ducts and is returned as chromic acid to the bath.

We have three round copper bars over the bath running lengthwise, one close to each side and the other in the middle. The two outside bars supply the current to the anodes, which also are 6% Antimony Lead, and the middle bar is used as the cathode and support for the roller being plated. The bath is sufficiently long to accommodate two 42-inch to 45-inch rollers at one time and also long enough to take care of most Schreiner rolls.

The rollers are brought into the plating room on wheel trucks. A round steel bar equipped with cones, such as are used on center bars for etching, is inserted in it. The roll is hoisted by means of a chain falls suspended from a straight tram-rail and pushed over to a wooden sink which has two pairs of rubber covered wheels set on the bottom of the sink. The roller is rotated on these wheels while being cleaned. We clean by means of swabbing with Kali cleaner, an alkaline cleaning compound put out by the Rumford Chemical Works. This is made up about 2 oz./gal. in hot water. The cleaner is rinsed off with water before swabbing with a solution of Sodium Cyanide about 2 oz/gal. This, too, is rinsed off and the roller wiped dry with a clean cloth.

The roller is next hoisted by the chain falls, swung over the bath, lowered into it, and hooked up to the copper cathode bar which we have previously mentioned. The current is turned on and the plating allowed to proceed for 20 minutes to one hour. After the plating has been completed, the roller is hoisted out of the bath and rinsed, while still suspended over the bath, by means of a small stream of water. The chromic acid which is thus rinsed off returns directly to the bath. The roller is dried off and then is ready for use at the print machine.

Originally, this talk was supposed to deal only with the utility of chromium plated printing rollers, but it has been suggested that a word might be said concerning the chromium plating of Schreiner rolls as well.

Due to the fact that our plating equipment is not exactly satisfactory for the handling of all sizes of Schreiner rolls, and besides has been kept quite busy plating printing rollers, we have not had as much experience with Schreiner rolls as we would like. However, we have plated about thirty rolls and have had satisfactory results from about half that number. Without being able to quote definite and comparative yardages run by plated and unplated rolls, our calender men have been of the opinion that the plated roll lasted about three times as long as the unplated. We have had rollers run over two million yards of goods, covering a variety of width, which appeared to be about as good at the end of this yardage as they were at the start. Other plants, I have been told, have run upwards of five million yards on one plating. There seems to be little question in the minds of the men who have used the plated rollers as to their utility. Besides the wearing qualities of the plated rollers, there is a resistance to corrosion, when a roll is exposed to dampness in a cold room, that appeals to calender men.

As you have no doubt gathered, we are extremely enthusiastic about chromium plating as a printing aid. We have had such excellent results from its use that we would not hesitate a moment to recommend it highly to anyone using copper printing rollers.

Discussion

(During the discussion which followed the presentation of his paper, Mr. Dick was assisted in answering questions by Mr. Gaunt of United Chromium, Inc.)

Q. Do you have any difficulty in removing the plating when you want to re-engrave?

A. (Mr. Dick). None, whatever. The chromium is very soluble in hot muriatic acid. The roll is heated with steam and then revolved in 10% muriatic acid. It takes only about a minute or a minute and a half, and has no effect on the copper.

Q. What kind of lint doctor do you use?

A. (Mr. Dick) We use a composition blade, but we have used steel. When we first started in with chromium plating rollers, we thought we got a good deal of excessive wear on lint doctors, but we got it on our cleaning blade as well. Some of this was undoubtedly due to poor plating. At the present time I would say that we have very little wearing down of either the cleaning blade or lint doctor.

Q. What per cent coverage do you get on drapery patterns?

A. (Mr. Dick) Up to 100%.

Q. Do you do light colors and do you have trouble with them?

A. (Mr. Dick) We do anything, from very light colors to black. We do have trouble with printing steam black.

Q. How often do you use your chromium plating plant?

A. (Mr. Dick) We use it every day in the week.

Q. Do you do any discharge work?

A. (Mr. Dick) No, we do not.

Q. Can you give us any information as to the cost of chromium plating, such as current, labor, etc.?

A. (Mr. Dick) No, I am not in a position to quote figures on the cost of chromium plating, except in a general way. It can be expensive or inexpensive, depending on the number of rollers plated, method of plating, etc.

Q. When plating Schreiner rolls, does the part nearest the cathode get most of the plating?

A. (Mr. Gaunt) The part of the Schreiner roll nearest the anode would ordinarily get the heaviest plating, but in plating Schreiner rolls, we rotate them, thereby evenly distributing the plating.

Q. How thick is the plating?

A. (Mr. Gaunt) About 2 to 4 ten thousandths of an inch.

Q. What distance between anode and cathode do you recommend?

A. (Mr. Gaunt) About 6 inches.

Q. If you shorten this distance, what would the effect be?

A. (Mr. Gaunt) The plate would build up too much on one side.

Q. If you rotate the roller can you shorten this distance?

A. (Mr. Gaunt) Yes.

Q. What is the effect on the surface if you speed up your plating?

A. (Mr. Gaunt) No difference. The plate is just as smooth and bright as if rotated at a greater distance.

Q. Why is it not recommended?

A. (Mr. Gaunt) It is recommended. It's the cost of building a rotating machine that some people don't want to go into. We furnish a blueprint and recommend that all rollers be rotated. That's more up to the judgment of the concern in question.

Q. Is there any building up of the plate on the edge of the copper roller?

A. (Mr. Gaunt) No, not in the short time required to plate. If there was it could be easily removed.

Q. What sort of tool do you use to remove it?

A. (Mr. Gaunt) A file. As far as denting is concerned, the chromium plate is no better than the underlying copper. It will dent just as easily.

Q. How do you explain the failure of chromium plated doctor blades on plated rollers?

A. (Mr. Dick) Apparently, a plated blade has less resistance to corrosion than an unplated blade. Of course, chromium is plated in a crystalline form and, consequently, there are spaces between the crystals, which enables corrosive liquids to start corrosion on the blade. We have found it unsuccessful to plate steel doctor blades.

Q. You think it is impractical to plate doctor blades?

A. (Mr. Dick) We have never found it to work successfully on a steel blade. We have plated brass blades, such as are used in backfilling, and these have worked alright.

Q. What would you say about the possibility of 1,000 amps. against 2,000 amps. for ordinary work, and what would your daily production be?

A. (Mr. Gaunt) Using 1,000 amps., plating one roller at a time, you coud do about twenty-two rollers a day.

Q. With 2,000 amps., could you do forty-four rollers a day?

A. (Mr. Gaunt) The average is about 35 to 38.

NORTH CAROLINA STUDENT SECTION

The North Carolina Student Section had as their guest recently Mr. Harold Faust, Manager of the Greensboro Laboratory of the Ciba Co.

Mr. Faust addressed the senior classes of the Textile School in the morning, giving lectures on color matching, money value, nomenclature, laboratory problems and other things of interest concerning laboratory experiments of large dyestuff manufacturers.

In the afternoon, Mr. Faust devoted the entire session to demonstrating practical laboratory methods in color matching. The students did this work while Mr. Faust gave the directions.

While one section of the class was color matching, another section was dyeing skeins of yarn with vat dyes using the poling method, as used in some mills. The preparation of the stock vat and the consequent dyeing was performed under the direction of Mr. Faust.

Mr. Faust is one of the well known dye demonstrators in the South and his visit is one of the many, planned by the Student Section, of men best qualified to demonstrate practical methods of the theories taught in their courses in the college.

DAVID B. HARDIN, *Secretary,*
N. C. State College, Junior Section of A.A.T.C.C.

UNEMPLOYMENT REGISTER

For Members of the A.A.T.C.C.

At the last annual meeting it was suggested that the Association conduct an Unemployment Register for its members.

In accordance with this suggestion, members who are without employment at the present time should forward to the secretary a statement as to their qualifications and experience. This information will be placed on file and subsequently published in these pages. Identifying key numbers will be used so that each case may be brought most effectively to the attention of those persons likely to be in need of men of the stated qualifications.

Employers are also requested to file with the secretary any opportunities which are available in their businesses.

It is to be understood that this Unemployment Register is not (at the present time, at least) to be used for the benefit of those now employed and who are anxious to improve their conditions.

A. NEWTON GRAVES,
Secretary,
c/o Franklin Process Co.,
Providence, R. I.

CALENDAR OF COMING EVENTS

Meeting, Philadelphia Section, May 27th, Whitemarsh Valley C. C., Chestnut Hill, Philadelphia.

* * *

Special Meeting, South Central Section, May 26, University of Chattanooga. Regular Meeting, May 27.

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Spring Meeting, Piedmont Section, usually held in April will be held about the middle of May.

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Annual Meeting, Chicago, Sept. 8th and 9th.

Proceedings of the American Association of Textile Chemists and Colorists

The Nation is Tied to Chicago's Fair

MANY of the older people of this and other countries were convinced that there never had been and never could be a World's Fair more complete and comprehensive than the great Columbian Exposition, which Chicago staged in 1893. Their conclusions were natural, based on the theory that the best couldn't be beaten. But they had evidently overlooked the fact that the best of the past was often to be found in the discard of the present.

At the time of the Columbian Exposition, Chicago had seen sixty years of progress. She had started her career in homespuns, had depended upon tallow candles for light and upon prairie schooners for transportation. It was a far cry from the primitive life of 1833 to the hustle and bustle of 1893. A new age had dawned. And Chicago celebrated. She built on her south lake front a gigantic white city—a veritable fairyland. It was "so beautiful, so wonderful, so gorgeous, so divine" that those who saw it have never forgotten it.

This replica of Fort Dearborn, one of Chicago's most thrilling historical monuments, was constructed on the shore of Lake Michigan at Twenty-sixth Street for the 1933 Century of Progress Exposition. Near here, a century ago, stood the original Fort Dearborn, and still nearer occurred in 1812 the massacre by Indians of the brave inhabitants of the Fort. The photograph shows, left to right, the officers' barracks, a corner of the blockhouse, the powder magazine, soldiers' barracks. The corners of two other barracks appear on either side of the picture.

But in harking back to the wonders of forty years ago, do not forget that the comforts, beauties and educational advantages of life have improved miraculously during the span of years between 1893 and 1933. And the Century of Progress Exposition will be as far ahead of the Columbian as present-day modes of living are ahead of those of the early nineties.

The Columbian was a play typifying America's rise from the primitive life of the pioneer; the Century of Progress is a great drama of modern human enterprise, whose historic drop-curtains and flies bring out the contrast between past and present. From every standpoint, the Century of Progress Exposition promises to be a World's Fair to which older citizens forty years hence will look back and stoutly declare, "It can never be duplicated! Its like will never be seen again!" There is little doubt but that history will repeat itself in that respect.

And, notwithstanding its enormous proportions, it has been established on the lake front downtown, where it may be reached from all parts of the city with equal facility.

Because Chicago is the world's greatest railroad center, you can easily dispose of the question of transportation. No spot on the Western Hemisphere can be reached with greater ease by the one hundred and twenty-three million people of the United States. Forty-two states have within their borders, cities and towns from which the railroads whisk their patrons to the heart of Chicago every twenty-four hours. And no matter what the direction from which the passenger hails, the "heart of Chicago" means a terminal within walking distance of that mammoth theatre on the lake front, in which the Fair is being presented.

Above all, don't forget that A.A.T.C.C. Convention headquarters are located in the "heart of Chicago." While we're enthusing about the prevailing attractions of the city in general, let us remind you of the particular plans being made for the personal entertainment of all you "Conventionites." The famous Congress Hotel is to be your home on September 8th and 9th. Your name on their records will be added to the most illustrious list of guests in history, including every President since Grover Cleveland.

Replica of Abraham Lincoln's birthplace in Hodgenville, Ky., which forms part of the Lincoln Group. The logs and timbers in this cabin are more than a century old.

SPRING MEETING, MID-WEST SECTION

THE spring meeting of the Mid-West Section of the American Association of Textile Chemists and Colorists was held at the Hotel Schroeder, Milwaukee, Wisconsin, Saturday evening, April 8th, 1933.

The business meeting was preceded by the usual informal dinner, eighty-two members and guests being present.

Mr. Carl E. Bick, Chairman, introduced Mr. Otto R. Hauser, Secretary to Mayor Hoan of Milwaukee, who welcomed the Association to Milwaukee and extended the hospitality of the city.

The minutes of the previous meeting were read and approved.

Mr. Berry, Treasurer, read the financial report which was approved.

Mr. Bick turned the meeting over to Mr. Eric F. Hempel, who had charge of arrangements for the Milwaukee meeting.

Mr. Hempel called for nominations for Councilor to represent the Mid-West Section on the Council of the Association.

Mr. Joseph Feit proposed the nomination of Mr. M. A. R. Selisch. Nomination seconded by Mr. Edward Morgan.

No further nominations proposed, chairman instructed secretary to cast one ballot.

Mr. Selisch accepted the office and thanked the members for the honor bestowed upon him and said that he would be glad to give his time and efforts to fulfill the duties of the office.

Announcement was made of the Annual Meeting of the Association to be held at Chicago, Illinois, Friday and Saturday, September 8th and 9th.

The following committees were appointed:

Publicity—Mr. A. T. Brainerd, Mr. E. A. Johnson.

Reception—Mr. A. J. Feit.

Entertainment—Mr. Elmer F. Smith.

Technical Papers—Mr. Gordon M. Markle.

It was decided to hold the Annual Meeting at the Congress Hotel, Chicago.

Mr. Hempel then introduced the speaker, Mr. Henry Eagar, manager of the finishing plants for the Standard Coosa Thatcher Co., who gave a very interesting talk on "Mercerizing."

Following his talk, Mr. Eagar answered the various questions which were submitted by the members.

A rising vote of thanks was given to Mr. Eagar.

Mr. Brainerd requested the members to give serious thought to the subject of technical papers, advising that it was not necessary for the writer to read his paper at the Annual Meeting. He requested members who had papers to offer to take them up with Mr. Markle, who was in charge of the technical program of the Mid-West Section and would cooperate with Dr. Powers, Chairman of the technical program.

He also suggested that some form of a button or badge be worn by all members of the Mid-West Section during the Annual Meeting at Chicago, in order to render information to visiting members from other sections.

The question of a summer outing was brought up and Mr. Edward Morgan offered the facilities of the Rochelle Country Club at Rochelle, Illinois, and advised we could have exclusive use of the club and golf course. Mr. Morgan's invitation was accepted and it was decided to hold the summer outing at Rochelle during June, the exact date to be announced later.

As there was no further business to be transacted, meeting was adjourned at 10:35 P. M.

Respectfully submitted,

FRANK J. ACKER, *Secretary.*

SPRING MEETING AND SUMMER OUTING, PIEDMONT SECTION

THE spring meeting of the Piedmont Section which has generally been held in the month of April has been postponed until the middle of May. At the afternoon session the following papers will be presented:

"Hosiery Dyeing and Finishing," by L. M. Boyd, Scholler Bros., Inc.

"Treatment of Water for Boiler and Textile Purposes," by C. D. Blackwelder, J. E. Sirrene & Co.

"Recent Developments in the Application of Fast Colors," by S. H. Williams, General Dyestuff Corp.

The program for the evening will be announced at a later date.

The summer outing of the section will be held on Saturday, July 1st, at the Mayview Manor, Blowing Rock, N. C. Special rates will apply for association members.

SOUTH CENTRAL SECTION ACTIVITIES

On May 26th the South Central Section will hold a special meeting at the University of Chattanooga. Alexander A. Guerry, president of the university, will preside, and Robert E. Rose, president of our Association will speak on "The Value of Research."

The meeting will be held in the Patten Memorial Chapel at the University and there will be invited all the chemists, engineers, business heads, civic and other organization officers in the vicinity.

In the morning Dr. Rose will also speak to the students of the Baylor School for boys, which is a well known preparatory institution.

The usual meeting of the section will be held on May 27th at the Hotel Patten and all the chemists in the neighborhood will be invited.

NOTE—*The remaining discussion on "The Moth—Friend or Foe," published in our last issue, will be held over until next issue.*

AMERICAN
DYESTUFF
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Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

A. P. HOWES, President
M. D. REESER, Secretary
H. F. CRAWFORD, Treasurer

Subscription price: $5.00 per year; Canadian $6.80; foreign $6.00

Vol. XXII May 8, 1933 No. 10

COMMERCIAL RESEARCH

DEPENDING upon the source of the financial support we might divide present day research into three divisions: private, academic and commercial. By private research we would include research financed by an individual for his own satisfaction or personal gain; academic research implies research carried on in educational institution by means of scholarships, endowments, grants of associations, etc. and by commercial research we mean investigations which are subsidized by companies who believe any resultant discoveries will accrue to their advantage or financial reward.

Of these different types of research we suppose that the first was that of the private investigator and dates back to the earliest of times and includes the old-time philosophers, alchemists, monastic workers and others of that type. This was later supplemented by work carried on in various educational institutions and hospitals which came into being. To the workers engaged in these two types of research we owe many of the discoveries of the laws of physics and chemistry. The latest type of investigation, commercial research, is of comparatively recent origin and is still being developed. Research of this type is typified by the work carried on in the laboratories of such companies as the General Electric Company, the Bell Telephone Company and, within our own field, the larger dyestuff and chemical companies.

One of the most recent of the modern commercial laboratories is that of Merck & Co. which was recently dedicated at Rahway, N. J. The importance of the occasion was shown by the presence of many of the prominent men of the day. Included among them were Lammot duPont, head of E. I. duPont de Nemours & Co., Sir Henry Dale of England who has been regarded as one of the foremost living pharmacologists of the time, Hugh S. Cumming, Surgeon General, U. S. Public Health Service and Josiah K. Lilly of the American Drug Manufacturers Association.

The contention has been voiced that royalties on patented products produced as the result of research are apt to interfere with the disinterestedness that is regarded as an essential of pure research. In refutation the question can also be raised as to whether research for the sake of discovery or invention in itself is of more value to humanity than research with financial gain as the ultimate goal. If one gives his work to the world and the other commercializes it have we any right to criticize either one?

When possible, unrestricted research is, we believe, more beneficial to the world and more satisfactory to the worker than research artficially curbed into certain narrow channels as directed by the financier. In this respect the remarks of Sir Henry Dale as given in his address at the above mentioned dedication are significant. He said that if necessity is the mother of invention then the spirit of investigation is its father. In the particular laboratory in question he brought out the fact that the workers were free to choose their own problems for investigation without being bound by the conditions of a personal endowment, as laudable as such may be. He urged unrestricted freedom in the furtherance of research and deplored a general use of patents if these tend to hinder progress.

It is not essentially true that pure research is lost sight of in the laboratories of commercial organizations and in substantiation we may cite the accomplishments of the Nobel prize winners, Langmuir, Bosch and Bergius who accomplished much while in the employ of commercial corporations. It is also true that certain types of research are most ably conducted with the financial aid and equipment of our industrial laboratories. We might also say that most of the larger and more liberal corporations have found it best to let their research departments function by themselves. Even research in pure science will function if exploited by the use of patents.

The above remarks, of course, apply to the functioning of the commercial laboratories. Conditions are different in other types of research as, for example, in the functioning of the research committee of the American Association of Textile Chemists and Colorists. Here there is no thought of personal or corporate financial gain.

However, the fact that we wished to emphasize when we started out to write and which we seem to have submerged in other thoughts is that commercial research is really coming into its own in all lines of industrial endeavor. Its importance to the success of so many undertakings is gradually becoming realized and fully appreciated. We are in favor of research whether its aim be to help people and incidentally cash in on any resultant profits or whether it be only to give to the world any significant discoveries. There are opportunities for both in our present commercial laboratories.

Textile Foundation News

Wearing Qualities

When one sock or stocking of a pair wears out considerably ahead of its mate, the wearer sometimes suspects the manufacturer of contriving to increase the consumption of his products. Fabric strength, however, is like that of the chain, and a weak link may develop anywhere from the textile fiber itself to the manufacturing processes, according to Lawrence B. Haley, Textile Foundation Junior Research Fellow.

A group of studies on textile strength and wearing qualities is being made at Alabama Polytechnic Institute, Auburn, Alabama, by Mr. Haley, who is working under the direction of Dr. H. B. Gordon. While this research is highly technical, its "dollars and cents" value is readily apparent to the general public.

The popular subject of fabric wear is one angle of Mr. Haley's investigation, which he explains in a report to Frank D. Cheney, director of the Textile Foundation, is planned "to improve the wearing properties of sheets, woolen goods, silk and rayon linings, upholstery and carpeting, and other commonly-used textiles."

Complementary to that project is an investigation of the relation between the strength of fibers and the strength of fabrics under varying conditions of wear.

"Fiber strength alone does not insure a strong fabric," Mr. Haley points out in his statement. "A hundred things may happen in converting the fibers to an article of utility, any one of which may bring disorder to normal expectancy. Good, strong fibers premise a quality fabric, but do not assure it. We are endeavoring to determine why the fiber of a respectable family may be perverted in strength of character while being developed into a useful member of the fabric society."

The third project in this research bears on one or two particular phases of mercerization. A mercerized broadcloth in the form of a shirt has some degree of merit in the eyes of the average man because it shines, Mr. Haley explains. The more femininely described attributes of sheen or luster are not acquired on this cotton fabric like a varnish but by chemical processes which change the structure and character of the cotton fiber.

"Proper mercerization, we know, strengthens cotton, improves its appearance and adds to its wearing quality," Mr. Haley concludes. "Our investigations, therefore, are to discover the proper degree of mercerization, the ideally correct chemical solution required, and accurate methods of controlling the process.

Scientific Research Aiding Textile Industry Development

Scientific research and business experience joined forces in the interest of the textile industry at a two-day conference in Washington (April 18-19) called by the Textile Foundation. Seventeen research fellows maintained by the Foundation at textile schools, universities and other institutions brought to the symposium a wealth of analytical data on their respective projects. These independent studies were splendidly coordinated and, by virtue of experienced suggestions from the Foundation Directors and Advisory Committee, guided into channels of greatest benefit to the textile industry.

Convening Tuesday morning at the headquarters of the Textile Foundation, the conference was opened by Franklin W. Hobbs of Boston, Chairman of the Foundation's Board of Directors. Mr. Frank D. Cheney of New York, a Director of the Foundation, presided at the morning session of the symposium and sounded the keynote of "research primarily to improve quality," which prevailed throughout the entire conference.

Much gratification was expressed by the Foundation Directors and Advisory Committee on the remarkable coordination and the practical application of research projects presented at both the morning meeting and the afternoon session, the latter being conducted by Stuart W. Cramer, Cramerton, N. C., Director and Treasurer of the Foundation.

Every one of the research reports was well received and evidenced unflagging pursuit of the problems assigned to the fellows. Particularly interesting in the Tuesday morning session was the related work on textile fiber structure and characteristics affecting fabrication, processing and finishing. Four of the research fellows, working independently as to method and place, are ferreting out the most intimate secrets of wool, silk, rayon, ramie and other textile fibers.

Donald R. Morey, Cornell University, is employing the rather unique method of polarized light phenomena to discover the micellar orientation in textile fibers. Using dyes which fluoresce and which attach themselves to the micelles in a definitely oriented manner, he determines by microscopic examination the direction of the polarized light and thereby the orientation of the textile fiber cells. Wayne A. Sisson, University of Illinois, using the X-Ray, G. Gordon Osborne, Massachusetts Institute of Technology, by microscopic study of fiber casts, and Raymond L.

Steinberger, Harvard University, in an analysis of plastic and elastic properties, are developing different phases of related problems.

Another report which drew considerable interest was that of Orrin W. Pineo, also of Massachusetts Institute of Technology, who through the development of spectrophotometric measurements hopes to catalog accurately any color combination. Referring to the limitations of eye-matching, where type of light is a deceptive factor, Mr. Pineo said he hopes to make it possible to transmit textile patterns by mail, telegraph or cable as spectrophotometric color curves.

Others in the series of illuminating discourses were: "Strength and Wearing Properties of Textile Fabrics," by Lawrence B. Haley, Alabama Polytechnic Institute; "Critical Study of Manufacturing Processes," by Roland L. Lee, Jr., Lowell Textile Institute; "Influences of Protein Constituents on Wool Fibers," by Wilber O. Teeters, University of Illinois; "Effect of Bacteria and Vegetable Oils on Silk," by Alfred N. Rogers, Lehigh University; "Micro-Biology of Textile Fibers," by Bryce Prindle, Massachusetts Institute of Technology; "Disposal and Recovery of Textile Wastes," by Maxwelton S. Campbell, University of North Carolina; "Chemistry of Dyes," by Herbert E. Ritchey, University of Illinois; "Protective Effects in Textile Deterioration and Dye Fastness," by Donovan J. Salley, Princeton University; "The Carbonization Process and Its Effect on the Dyeing Properties of Wool," by Bertil A. Ryberg, Lowell Textile Institute, and "Adsorption and Absorption of Solutions by Textile Materials," by John B. Calkin, Cornell University.

William C. Smith, working on methods for standardization of tests of fastness to light of colored textiles, and Milton Harris, studying the relation between electric charges on textile fibers and their dyeing and processing characteristics, are research associates of the American Association of Textile Chemists and Colorists stationed at the Bureau of Standards. Their work is supported in part by the Textile Foundation and their reports were presented to the conference.

Results of the Tuesday sessions were summed up and the reports discussed by Dr. E. R. Schwarz, Professor of Textile Technology, Massachusetts Institute of Technology; Dr. H. S. Taylor, Head of Frick Chemical Laboratory, Princeton University; and Warren E. Emley, Chief, Divisions of Organic and Fibrous Materials, U. S. Bureau of Standards. Dr. Robert E. Rose, Wilmington, Del., and Dr. E. W. Camp, Head of the Textile School, Alabama Polytechnic Institute, also addressed the symposium.

Dr. Lyman J. Briggs, Director, U. S. Bureau of Standards, and Dr. Henry G. Knight, Chief, Bureau of Chemistry and Soils, U. S. Department of Agriculture, spoke to the group at the Tuesday evening session. Both speakers upheld the value of research and commended the work of the Foundation Research Fellows.

The Wednesday program of the conference was arranged by W. E. Emley and W. D. Appel of the Bureau of Standards and included a tour of that Bureau and other scientific offices, whose equipment or findings might facilitate the work of the research fellows. Bureau of Standards investigations on adsorption and desorption, hydrogen ion concentration, elastic and plastic properties, iso-electric point of textile fibers, quantitative analysis of textiles, microscopic and photomicrographic observations and color fastness tests were demonstrated, and the cotton mill operated to the considerable interest of the group.

The National Academy of Sciences, Bureau of Agricultural Economics and the Fixed Nitrogen Laboratory of the Department of Agriculture were other points of interest on the inspection tour, conducted by Emley and Appel.

The Textile Foundation was incorporated to promote "scientific and economic research for the benefit and development of the textile industry and allied branches including production of raw materials." The Board of Directors includes the Secretaries of Commerce and of Agriculture, and three other members; these now being Franklin W. Hobbs of Boston, Chairman; Stuart W. Cramer of Cramerton, N. C., Treasurer, and Frank D. Cheney of New York. Mr. E. T. Pickard, Secretary, is located at Textile Foundation headquarters, Department of Commerce, Washington, D. C.

A. W. Buhlmann, Inc., in New Offices

The firm of A. W. Buhlmann, formerly located at 200 Fifth Avenue, will now be known as A. W. Buhlmann, Inc., and is now located at 551 Fifth Avenue. They have distributed a booklet calling attention to the accomplishments of this firm from 1904 until today.

Application of the Acid Wool Dyestuffs

Sample card No. 977 of the Society of Chemical Industry in Basle contains 387 dyeings on wool piece goods with the known Acid dyestuffs and the Cloth Fast Colors of this company.

The compilation and layout of this new sample card is especially fine and practical. The fastness tables as well as a short description of each individual dye are adjacent to the dyeings, so that the dyer is in position to comprehend at once the strength, shade, fastness and application of each separate dyestuff.

Furthermore, the different dyeing processes are described and the dyes classified according to their properties and applications.

Determination of Acids in Wool

(Continued from page 304)

wool contains sodium sulfate this is included with free acid. When washing is carried out as described above the results are good.

Neutral wool was dyed with Erio Anthracene Blue with 5% sulfuric acid and 20% Glauber's salt, washed and dried. The residual acid was then determined by the three methods. The percentages found were—

	1st Lot	2nd Lot
(1) Triethanolamine	2.15	2.01
(2) Sodium bicarbonate	2.05	2.05
(3) Magnesium carbonate	2.00	1.96

When dyed samples are treated with sodium bicarbonate or triethanolamine, titration is often difficult owing to the color of the extract. This stripping action can be minimized by the use of a saturated solution of sodium chloride instead of distilled water. In the second experiment given above, the result obtained when using sodium chloride was 2.11%.

Woodmansey's Method (*loc. cit.*) is based upon the distribution of the acid between two immiscible solvents, viz. wool and water. When 0.05% solution of Methyl Red in dilute alcohol is spotted on cloth, a distinct indication of acid is only given when the cloth has been treated with 0.2% sulfuric acid and dried, proving that wool is essentially alkaline. For the determination of acid in a sample of woolen cloth, standard curves must first be established for a similar neutral cloth which has been treated with known quantities of acid. Pieces of the neutral cloth (10 g.) are each steeped in 300 c.c. of solutions made up with increasing quantities of standard sulfuric acid. After standing over night, 250 c.c. are withdrawn and titrated. The curves are plotted with total acid as ordinates and acidity of 250 c.c. of aqueous solution as abscissæ. Similar determinations are carried out with the sample to be tested, three pieces being taken, one with water and two with known quantities of acid. By superimposing the curve of the sample on that of the standard, the equivalent of acid already present in the former is found by difference. When the net acidity is required, it is necessary to determine the amount of acid required to neutralize the wool and deduct this from the total value found. There are obvious difficulties connected with this method apart from the fact that a sample of the acid-free cloth is rarely available.

The Terephthalic Acid Method—This method (Hirst and King, *loc. cit.*) is very reliable. A weighed quantity of the wool is treated with a known volume of sodium terephthalate solution, warmed to 60° C. and allowed to stand for 3 hours. The solution is poured off, the wool washed and pressed several times with water, and the united liquids filtered. A known excess of N/10 sulfuric acid is then added, the liquid again filtered, and the filtrate titrated with N/10 sodium hydroxide with Bromophenol Blue as indicator. Calcium soaps, if present, must be determined and allowed for.

The Sodium Acetate Method—When wool containing a mineral acid is treated with a solution of sodium acetate, an equivalent quantity of acetic acid is liberated. Although this acid cannot be removed easily by washing, it can be separated by distillation with steam. If these facts could be applied to the analysis of wool, all difficulty due to adsorption or stripping in the case of dyed samples would disappear. It was found that for quantities of acid usually present in 2 g. wool, the whole of the liberated acetic acid is recovered in about 650 c.c. of distillate. The apparatus used consists of a 500 c.c. distilling flask connected to a steam generator and a condenser. The water in the steam generator is made faintly alkaline with lime water or sodium hydroxide to fix carbon dioxide and boiled for a short time before connecting to the distilling flask to expel air. About 2 g. of the sample to be tested are weighed into the distilling flask, and a little water and from 0.5 to 1.0 g. sodium acetate added. Steam is then passed through the flask until 650 c.c. distillate have been collected. The distillate is titrated with N/10 sodium hydroxide in presence of phenolphthalein. Not only does this method overcome the errors due to adsorption, but it simplifies the determination of acidity, since it obviates the necessity for repeated washing and, after starting, requires no further attention.

The accuracy of the method was tested by distilling a measured volume of N/10 sulfuric acid with sodium acetate, and also by means of a blank test with sodium acetate and water. It is very important that the water in the steam-can should be made alkaline as described. When ordinary tap water is used, the bicarbonates present give off sufficient carbon dioxide to affect the result. It was found also that 650 c.c. distilled water obtained in this way require 0.4 c.c. of N/10 sodium hydroxide to produce a color with phenolphthalein, and this amount should be deducted from the total alkali used. Some of the results obtained are given in the following table:

	% H_2SO_4 with Triethanol-amine	% H_2SO_4 with Sodium Bi-carbonate	% H_2SO_4 with Sodium Acetate	% H_2SO_4 with Magnesium Carbonate
Purified wool.	0.11	0.07	0.09	...
			2.01	
	2.01	2.11	2.05	
Dyed wool....				1.96
	2.08	1.96	2.18	
			2.20	

The use of the sodium acetate method for dyed samples is very satisfactory, since no colored extract is produced.

Acetic Acid, Formic Acid, and Sulfurous Acid—When either acetic or formic acid is present the acid can be distilled off directly with steam and titrated.

Sulfurous acid can be determined also directly by distillation with steam into either hydrogen peroxide or bromine water and precipitating the sulfuric acid formed with barium chloride. Since sulfurous acid may be present as sulfite it is better to add a little hydrochloric acid to the contents of the flask before distilling.

The Calcium Carbonate Method—Practically every acid which is likely to be present in wool would liberate carbon dioxide from calcium carbonate, and experiments were made in which sodium acetate was replaced by precipitated calcium carbonate. Since making these experiments we have found that Woodmansey (*loc. cit.*) attempted to determine acid in wool by boiling it with a weighed piece of Iceland spar and calculating the acidity from the loss of weight. Apparently his experiments were not successful. Although a piece of Iceland spar did not act satisfactorily, it was thought that precipitated calcium carbonate, having a much larger surface area, might do so.

In the first experiments the wool was wet with water, a little calcium carbonate added and distilled with steam into a measured volume of standardized barium hydroxide solution. The carbon dioxide was then determined by titration with N/10 acid in presence of phenolphthalein. The results obtained in this way were always higher than those given by the other methods mentioned, although every precaution was taken, and it was found that the rate of distillation affected the result. This suggested that possibly gradual hydrolysis of the wool occurs with the liberation of carboxyl groups which decompose calcium carbonate. A method similar to that used in the Kjeldahl process was then tried and found to give practically the same results as the sodium acetate and other methods. Two g. of the sample were placed in the Kjeldahl distilling flask, and some carbon dioxide-free distilled water and precipitated calcium carbonate added. The mixture was boiled for 15 min., the end of the delivery tube dipping beneath the surface of a known volume of standardized barium hydroxide solution. The receiving flask was connected to a trap to prevent access of air. The carbon dioxide was determined by titration with N/10 acid in presence of phenolphthalein and also by titrating the barium carbonate formed. The latter method has the advantage that the exact strength of the barium hydroxide solution need not be known. It is carried out in the following manner—phenolphthalein is added to the cooled distillate and then N/10 alkali until a faint pink color is produced. N/10 acid is next added, drop by drop, until the pink color is just discharged. A known volume (e.g., 50 c.c.) of N/10 hydrochloric acid is now added and the mixture warmed gently or allowed to stand for half an hour to decompose the barium carbonate, after which the unused acid is determined by titration with N/10 sodium hydroxide solution in presence of Methyl Orange.

The method was checked by means of a blank experiment with water, calcium carbonate, and known quantities of sulfuric acid. The figures given in the following table show that the method is reliable and gives results comparable with those obtained in other ways.

Exp.	% H_2SO_4 by direct titration $Ba(OH)_2$	% H_2SO_4 by titration of $BaCO_3$	Mean % H_2SO_4 by Sodium Acetate	% H_2SO_4 by Sodium Bi-carbonate	% H_2SO_4 by Triethanol-amine
1	1.99	...	...	...	...
2	1.98	...	...	...	...
3	2.08	2.08	...	...	...
4	2.13	2.00	2.08	2.03	2.07

If the distillation is continued for more than 15 min. higher results are obtained. This is illustrated by the following experiments. Two g. of acid wool were distilled in the manner described for 15 min. and the distillate titrated. More water was then added and the mixture distilled again for 10 min., the distillate being titrated as before. The results obtained were:

Exp.	% H_2SO_4 1st distillation	% H_2SO_4 2nd distillation	Total H_2SO_4
1	2.00	0.29	2.29
2	2.13	0.14	2.27
3	2.00	0.17	2.17

The effect of more prolonged boiling was tested. Two g. of purified wool were distilled with calcium carbonate for 15 min. and the evolved carbon dioxide determined. More water was then added to the contents of the flask and distillation repeated. The results obtained were:

	% Acid as H_2SO_4	Total Acid
First 15 min.....	0.51	...
Second 15 min.	0.36	0.87
Third 15 min.....	0.26	1.13
Fourth 15 min.....	0.27	1.40

The residual liquid in the distilling flask contained traces of sulfides and dissolved protein. A weighed quantity of the purified wool was then boiled with distilled water for 6 hrs. under a reflux condenser. Some sulfuretted hydrogen was given off, but no change in the pH of the liquid could be detected by means of indicators. After boiling for 6 hrs., calcium carbonate was added and

(Continued on page 319)

Rayon Dyeing and Finishing—5

By **B. L. HATHORNE**
Consulting Textile Chemist

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(Continued from page 294, April 24th issue)

CHAPTER V—DYEING AND FINISHING OF CIRCULAR KNIT RAYON FABRIC*

Discussion of Greige Goods

Knitting Oil

In order to produce a smooth, pleasing stitch, without excessive waste, it has been found necessary to apply a very considerable amount of oil to rayon before the knitting operation. At the present time, practically all circular knit rayon fabric is sent to the dyehouse containing between 6% and 15% of oil, based on the weight of the fabric as received.

Unfortunately, much of the yarn coned for the knitting trade is oiled with the cheapest oil that will facilitate the coning operation and give sufficient lubrication to enable the knitting machines to run at top speed. Such oils usually consist of very low grade mineral oils (which often contain an appreciable amount of very thin comparatively volatile oil to increase penetration) mixed with small percentages of animal and vegetable oils such as red oil, neatsfoot, degras, olive oil, etc.

It is very well known that all vegetable fibers are very readily attacked by even the mildest acids when the same are allowed to remain in the fiber for a considerable period of time. Few knitters, however, appreciate the fact that the saponifiable oils and fats used as rayon lubricants develop into weak organic acids on the fiber. Such materials will inevitably weaken rayon when allowed to remain in contact with the same for an appreciable period of time, particularly when the fabric is stored in a humid atmosphere.

Some knitters believe that fabric is absolutely stable to storage when one hundred per cent neutral mineral oil is used for lubricating purposes. They assume that mineral oil is an absolutely inert chemical compound and cannot affect vegetable fibers in any way. Nothing could be further from the truth. Many of the cheap mineral oils contain an appreciable percentage of oxidizable matter. Such oils develop acidity by oxidation when oiled greige goods are stored for an appreciable length of time.

The question may well be asked—why it is that rayon oils do not cause more trouble than at present, if they are as dangerous as indicated. The answer lies in the fact that the turnover of knitted fabric is so great that fabric is rarely ever allowed to stand for any considerable length of time in the greige state.

When business conditions are such that knitters suddenly curtail production, it sometimes happens that knitted fabric is stored in the greige for an appreciable period of time under disadvantageous conditions. It is at such times that rayon oils attack and injure circular knitted fabric.

The weakening that takes place during storage is never sufficient to cause the fabric to appear materially weaker in the dry state. It is only when the fabric reaches the dyehouse and is put into a wet condition for scouring purposes that the trouble becomes apparent.

"Graphite" Marks

Circular knit rayon fabric often contains very objectionable black marks, known as "Graphite" marks, which are caused during the knitting process. The word "Graphite" is entirely misleading, as these marks are often caused by iron oxide, which is continually rubbed off by the action of the moving parts. Quantities of this objectionable iron oxide accumulate rapidly on knitting machines when the same are not properly cleaned. Carelessness on the part of the operators then allows such accumulated deposits to become attached to fabric or yarn during knitting.

"Graphite" marks cannot be removed from fabric by any ordinary scouring procedure. If there are only a few such spots in a large batch of goods, the simplest procedure is to dip the spots into hot soapy water and rub them slightly by hand.

When such marks are found throughout the entire machine load of fabric, the only feasible way of removing the same is a treatment with oxalic acid. This treatment is relatively costly, and very dangerous to the fabric if not properly controlled—so should be avoided whenever possible.

* It will be noted that we are publishing Chapter V prior to Chapter III and IV. This will not interfere with the continuity of the series as each Chapter is a complete subject in itself.

When an oxalic acid treatment is found necessary, the operator should proceed in the following manner:

(1) Scour as usual.

(2) Rinse free from all soap.

(3) Prepare a clear water bath at 160° F.

(4) Add 2% Oxalic Acid to the bath.

(5) Run until "Graphite" marks have disappeared, taking care not to work in this bath longer than twenty minutes.

(6) Rinse carefully and proceed as usual.

Sinker Marks

Finished circular knit fabric sometimes shows longitudinal marks, or streaks running throughout the piece. These marks are often blamed on the dyer, although they cannot be caused or prevented by him.

In order to cast off the loops during the knitting operation small moving parts called sinkers are used. These parts wear very rapidly and should be replaced when they become excessively worn. As this operation takes considerable time and as the cost of material alone amounts to about $15.00 per machine, knitters often run a set of sinkers much longer than they should, even though they realize that by so doing they are making inferior fabric. These old unevenly worn sinkers cause tight and loose stitches, thus forming longitudinal marks throughout the fabric.

Bent and worn needles and worn cylinder slots cause the same sort of defects to appear. However, regardless of the cause, the lines are always called "sinker marks."

Knitters often attempt to blame the dyer for sinker mark defects. A dyer should not accept blame for the failure of the knitter to properly care for the machines.

Uneven Stitch

Knitting machines continually get "out of balance" due to a number of reasons. When they are allowed to run in this condition a very unevenly stitched fabric results. The tight or loose stitch resulting from this unbalanced condition causes a slight change in the apparent luster of the particular stitch involved. This variable luster at first glance appears to be a variation in color and is practically always blamed on the dyer. Close examination of the finished fabric will disclose the presence or absence of uneven stitch.

"Light" and "Heavy" Ends

It sometimes happens that one end of a rayon skein will consist of a lighter or heavier denier than the balance of the skein. Such light and heavy ends show up very plainly in the finished fabric, and to the casual eye give the appearance of uneven dye application. Again, careful examination will quickly show the true cause of the trouble.

Sulfur Spots

The viscose process of rayon manufacture sometimes results in the production of so-called sulfur spots. These are small weak spots in the yarn and are usually accompanied by small quantities of free sulfur. Such spots are usually strong enough to pass successfully through the winding and knitting operations, but do not have sufficient strength to pass through the dyeing process.

Unfortunately, the scouring process which causes the sulfur spots to become evident usually destroys the minute traces of free sulfur, which would, when present, allow the dyer to definitely prove that the trouble is due to improper rayon manufacture rather than to improper scouring and dyeing procedure.

Luckily, sulfur spots have a characteristic appearance, which is at present well known throughout the trade, and which is accepted as evidence of so-called sulfur spots. This eliminates the necessity of definite proof on the part of the dyer, and is usually sufficient to absolve him from blame.

(*To be continued*)

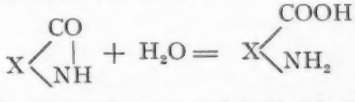
DETERMINATION OF ACIDS IN WOOL

(Continued from page 316)

the mixture distilled into barium hydroxide solution for 15 min. The results of these experiments gave:

Original wool ... 0.29% acid (calc. as H_2SO_4)
After boiling .... 0.95% acid (calc. as H_2SO_4)

The explanation of this increase in acidity towards calcium carbonate may be that bound carboxyl groups are made free by hydrolysis, thus:



This action of water was tested further in the following manner—1.23 g. of purified wool was boiled with water for 14 hrs. under a reflux condenser connected to a wash bottle containing lead acetate solution. After boiling for 30 min., sulfuretted hydrogen was given off; at the end of 14 hrs. a copious precipitate of lead sulfide was present in the wash bottle. This was collected, washed, dissolved in nitric acid, and the solution evaporated to dryness. The residue was dissolved in water and the lead determined colorimetrically. This, converted into sulfur, amounted to 0.5% of the wool taken. The liquid in the flask gave a market biuret reaction. Its pH was approximately 6.5. It was tested for the presence of amino-acids by the formaldehyde method, but none was found. The boiled wool had a distinctly greater affinity for Methylene Blue than the original sample, which may indicate the presence of free carboxyl groups. Since very few references can be found to the action of water on wool, it is proposed to continue these experiments.

Technical Notes From Foreign Sources

Artificial Fibers Containing Nitrogen

Fritz Ohl—Kunst-Seide 13, 347 (1931).—The idea underlying the synthesis of artificial fibers is older than many would suppose. Apparently, the first known proposal for the generation of such fibers originated with the famous English physicist Hooke, in 1655. His idea, involving the use of glutinous material as the basic substance (possibly glue itself) fell at that time upon barren ground. In those days, the wool industry held the field, as a kind of national industry, to be protected at any cost. In 1734, Reaumur proposed the spinning of fibers from solutions of gums of various sorts. This proposal also came to nothing, although the idea has reappeared in some modern patents. Gums, caoutchouc, latex, etc., are involved in some of these recent patents, though often in company with cellulose itself. E.g., E. P. No. 328,627, of 1930 (Dreaper) describes the production of fibers from cellulose solutions, to which has been added latex. The spinning takes place according to the wet process, the sulphur liberated being retained incorporated in the fiber. Thus, by incorporation of some accelerator, such as diphenyl guanidine, during the washing process, the fiber can finally be vulcanized at a temperature of 90° C. Other patents, of about the same period, employ elastic or unelastic polymerization products of the butadiene series (these working up toward caoutchouc), or derivatives of caoutchouc itself. The product, after spinning, etc., can be dyed, weighted, finished, and worked up alone or in mixture or union with wool. It is claimed that such fibers are satisfactorily fast or resistant toward high temperatures, water, chemicals of the ordinary sort, as HCl or NaOH, organic solvents, weathering, etc., and are of excellent luster. But all such proposals are apparently, up to now, unfilled industrially. They are, however, without doubt of great interest.

The artificial fibers now recognized as practical products are all based upon cellulose as the fundamental substance, and apparently this cannot be replaced by anything else. They have won and are maintaining a position which has not meant replacement of the natural silk, but which exists parallel to it and on its own level, as an independent fiber of value. All of the artificial fibers then, differ radically from true silk in the fundamental substance composing them.

Though up to now it has not proved possible to produce a fiber equivalent to true silk chemically, yet this possibility has not been abandoned, for it is perfectly clear that the fundamental substance involved is of decisive importance in its influence upon the properties of the resultant fiber. Obviously enough, the widely different chemical nature of artificial and of natural silk is responsible for the presence or the absence of the different physical and chemical properties of the fibers—properties which are deplorably absent in artificial silk as we at present know it. In order to produce a fiber really similar to natural silk, one must transform a substance or mixture, either of albuminoid nature or containing albuminoid substances, into a fiber. From the chemical standpoint, the N-content, and the manner in which the nitrogen is combined, will be decisive as to the properties of such a fiber. Even such natural fibers as wool belong to the same group as does silk, i.e., are built up of albuminoids; but all vegetable fibers are simply cellulose.

The fineness of any kind of fiber is the first point of value. But the influence of the chemical substance forming the fiber is also of importance, especially in reference to the nitrogen content. Nitrogen influences favorably not only the fiber's affinity for dyestuffs, but also has its own influence upon physical properties, especially its tensile strength, ability to stand the strain of knitting, its resistance to boiling, its heat-insulating powers, etc. Of these, even the affinity for dyestuffs alone increases our interest in the possibility of producing a fiber containing combined nitrogen, especially when we think of the continuously changing demands of fashion, and the possibilities which an entirely new sort of fiber would present. It needs hardly more than mentioning what advantages in dyeing are possessed by a fiber containing nitrogen, and what variations in the mode of dyeing would be possible when such a fiber was combined in the weave with the already known cellulose or cellulose ester fibers. Even the "homoeopathic" nitrogen content of a nitrate silk, for example, a content of perhaps 0.05%, increases the affinity of the fiber toward dyestuffs in a remarkable way, as compared to the affinity of a pure cellulose or cellulose ester fiber.

As to physical properties of such fibers, it has been known for some time that a nitrate fiber possesses a remarkable tensile strength before its denitration, and that the loss in tensile strength upon denitration is far greater than would be expected from the accompanying loss in weight of substance; also, that a cellulose acetate fiber containing a certain amount of cellulose nitrate displays a noteworthy superiority in tensile strength. But such facts do not point to a solution of the problem from the practical side, on account of the dangerous combustibility of cellulose nitrate.

In addition to increased affinity for dyestuffs, thus greatly broadening the possibilities along color lines, and the mechanical advantage gained by increase in tensile strength, it should be considered further that a fiber of nitrogenous nature would display other properties also, which should bring it still closer to natural silk; for example, the property of felting together of the fibers, a

property wholly lacking in our present artificial fibers. Of course, it is possible to modify a cellulose or cellulose acetate fiber, during its spinning, in such a way that its surface is no longer smooth, but striated or crisped or rough, or even scaly. It ought then to be possible to carry this modification so far that the resultant fiber should felt together as characteristically as wool. And, beyond this property of roughness and "feltability" of fiber, there is the matter of hygroscopicity of fiber to be considered. The author speaks of an artificial fiber given to him for examination, which consisted of cellulose acetate, upon the surface of which a very thin layer of hardened gelatine had been coated. This fiber naturally displayed interesting affinities for dyestuffs, and, because of its strongly roughened surface, a tendency to felt; and was being regarded with great interest by certain felt-manufacturers. Such a fiber, however, has apparently not yet been placed upon the market in detectible amounts. (An acetate fiber can easily be produced which, by wet-spinning in a suitable bath, will come out with as rough a surface, and will then be capable of felting; but the advantages of its content in nitrogen will, of course, be lacking.)

Naturally, attempts have been made to spin nitrogenous fibers from gelatine, glue, casein, etc. One of such products produced from gelatine, was actually marketed for a short time under the name Vandura silk. But such fibers consists only of chemically degraded and depolymerized proteins; and any degradation of substance, whether of albumen, cellulose, or any other material, displays a similar degradation of properties, or at least of decisiveness of properties, of fibers spun from it. The conversion of such substances into a "spinnable" form, and the regeneration of them as a fiber, necessarily involves such degradations; the original substance is really not regenerated at all. The possibility of producing a really valuable nitrogenous fiber from such substances, at least, according to any method yet proposed, seems to be absolutely excluded. Even were this particular difficulty avoidable, the processes, as they stand, involve such technical difficulties as tedious preparation of the spinning solution, complicated conditions to be maintained in preparing and using the spinning bath, complicated aftertreatments, etc., all of which would make the processes commercially unprofitable. The only nitrogen-containing fiber manufactured today, at least in the proper sense of the word, is nitrate-silk, with its very minute and accidental nitrogen content; and its nature, satisfactory or unsatisfactory in the various characteristics, is well known.

Procedure similar to these found to be unsatisfactory for the use of proteins have been employed with high-molecular proteins, such as collagen, keratin, hide-substance, etc. Even with these, i.e., starting with such higher-molecular complexes, some degradation must occur in bringing them into solution for spinning, and precipitating them by spinning. There is only some gain, perhaps, in the fact that their much greater molecular weight, to start with, may involve, e.g., a degradation of 50% in complexity, to choose a hypothetical figure for the sake of definiteness, this might still mean that the final product, the spun fiber, would or at least could be of greater molecular complexity than the glue, casein, etc., employed as the starting point in the processes already mentioned, and thus far ahead in molecular weight of the fibers spun from these simpler proteins. The actual degree of degradation, however, would seem to be essentially much less than above; and such a fiber would approximate the ideal synthetic nitrogenous fiber much more closely in its properties than anything yet produced. Bergmann of Dresden has taken out certain German patents (notably Nos. 442,520 and 445,503) dealing with this avenue of approach. The first of these patents considers the solution and reprecipitation of collagen or gluten. The solvent is a solution of copper or nickel oxide in ammonia-water. The dissolved protein is easily reprecipitated by acids or appropriate salts. Bergmann mentions the possibility of mingling cellulose with the proteins, thus producing fibers of distinctive properties and affinities. The second patent mentioned covers the use of keratins, which appear to dissolve in the above metallo-ammoniacal solvents without much change, and which can of course be reprecipitated as before, in the spinning-bath. The possibility of incorporating cellulose in this process is also mentioned by Bergmann.

Heberlein and Co. of St. Gall have chosen such substances as horn, animal hide, tendons and sinews, and even silk or wool, as the starting point of their method. The patents involved (F. P. No. 669,634 and E. P. No. 306,464) claim that the viscous solutions prepared from such substances can be spun in the customary manner according to the wet- or dry-spinning processes. But the spinning certainly involves difficulties. The materials are introduced into 10/1 their weight of fused phenol, and the material allowed to swell in this by gradual raising of the temperature, until complete solution takes place. Such a solution might well occasion difficulties in spinning. (Phenol has also been proposed as a solvent for casein.) Even were such difficulties surmountable, it would be difficult to remove the odor of the phenol completely from the fiber.

Waste silk and vauleless by-products of natural silk have of course been drawn into the circle. Several patents have been issued which are based upon the use of such substances, but are of no practical value. Even the soft constituents of the silkworm itself have been proposed for use as the fundamental material. Even those processes which depend upon the use of natural silk waste have never gotten beyond the laboratory stage. The difficulties encountered are too great for technical use; the method of getting the raw stock into solution without too much degradation of the molecular structure, the trouble of keeping the solution stable for a reasonable time, the undue length of the spinning bath, etc., and the slowness of the precipitation which is requisite, all make

the processes merely interesting laboratory methods, or even only curiosities.

The author believes that the already-mentioned method, that of producing cellulose or cellulose acetate fibers with an actual content (not coating) of nitrogenous substance, does offer possibilities. Only, such a nitrogenous component must be one which brings with it advantages, and no disadvantages. A casein fiber with a cellulose acetate admixture (F. P. No. 354,942) is as little valuable as a cellulose acetate fiber with a cellulose nitrate content. For, again, apart from the actual possession of valuable properties, it is required that the whole process of production be not too complicated, and that the required working conditions be such that they can easily be kept within. Special aftertreatments, like the hardening of coats of gelatine, etc., are not allowable on technico-financial grounds.

He believes that a cellulose acetate fiber with a nitrogenous admixture is of the greatest promise and possibilities. By use of a suitable admixed component, it should be possible to employ primary cellulose acetate for the foundation of the mixture, which would mean that the fiber would possess greater tensile strength, the cellulose molecule being less broken down. Further, the whole saponification process requisite in the production of "cellulose acetate" as we know it would be unnecessary —time, trouble, money would be saved. The only doubtful point is, whether such a primary cellulose acetate with its definite solubility factors could be so influenced by admixture as to permit use of the solvents employed in the dry-spinning process.

There seem to be at present two possible prospects. One involves the use of cyanogen compounds as admixtures. Very little nitrogen is required to give the fiber the properties so much desired from the dyeing standpoint. Mixed acid and cyanic acid cellulose esters, containing nitrogen, therefore, have already been synthesized. Such compounds are claimed to behave, in spinning, like normal cellulose triacetate, and are miscible with its acid solutions in any proportion. The cyanide groups can, it is stated, be converted into cyanic acid groups, by use of alkali and hydrogen peroxide, under such conditions that the cellulose acetate is not altered. It has not yet been determined whether the cyanide groups should best be oxidized to the cyanic acid groups during the spinning, or in the spun material. The other possibility seems to be offered by the use of an admixture of a urea condensation-product, added to the spinning solution. Such condensation-products are soluble in the same media as are employed for cellulose acetate. The disadvantage seems to be, that such substances often have a tendency to cause precipitation of the cellulose acetate. But this trouble should not be difficult to surmount.

(The abstractor would, however, raise the point as to whether it can be expected that a fiber spun from a mere mixture, and so consisting of a rather neutral or inactive fiber intershot with particles or strands of the more reactive admixture, really will prove to have the desirable properties of a homogeneous fiber, in which the components of desirable nature are chemical and not merely physical components. It would seem to be necessary to accomplish some sort of actual combination of the components. That is, would not a fiber spun from a mixture with the components merely in each other's company, so to speak, be comparable to a fiber claimed to be a cotton yarn to which special desirable properties had been given, but which consisted only of a cotton yarn in which were present a small number of independent wool fibers, uniformly distributed, to be sure, but nothing more? This example would be of microscopic, the above-mentioned fibers of sub-microscopic nature, but the essential similarity of the two cases would seem to be valid.)

Stable Diazo Preparations (or Diazotizable Preparations)

German Patent No. 453,985 (27-XII-'27) — *I. G. Farben-Ind. A. G.*—These preparations contain, of course, a diazotizable amine (which contains no sulpho or carboxyl groups), an acid substance which can combine partly or wholly with the amino group of the base, a nitrite, and a solid diluting agent, in this case more or less characteristically a partly or wholly dehydrated magnesium chloride. This compound acts not only as a diluting agent, but as a stabilizer. Instead of magnesium chloride, one of its double salts may be used, or partly dehydrated aluminium sulfate, alum, or aryl-sulfonates.

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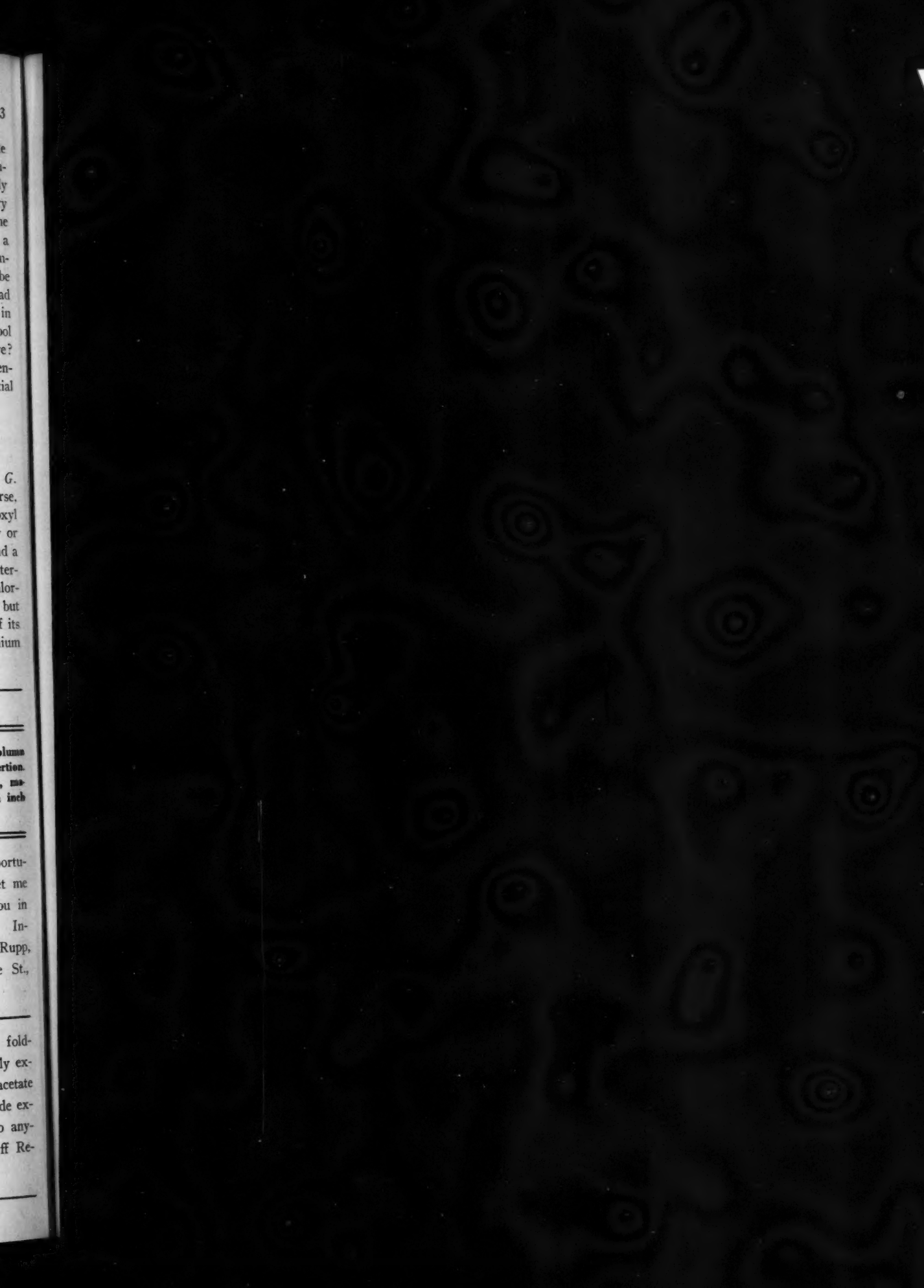
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